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Hazardous Waste Management. Proceedings of a
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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs, and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments, and the needs of both large and small businesses in handling their wastes responsibly and economically.

This Proceeding presents the papers and abstracts of presentations made at the International Conference of New Frontiers for Hazardous Waste Management. The U.S. EPA, NUS Corporation, National Science Foundation, and American Academy of Environmental Engineers co-sponsored this conference in order to summarize important new technological developments and concepts with broad international application.

David G. Stephan, Director
Hazardous Waste Engineering Research Laboratory

ABSTRACT

The International Conference on New Frontiers for Hazardous Waste Management was held in Pittsburgh, Pennsylvania, September 15-18, 1985. The purpose of this conference was to examine the state of technology for the disposal of hazardous waste. Emphasis was placed on papers that summarized important new technological developments and concepts with broad international application.

Sessions were held in the areas of: (1) Quantification of Health Hazards, and Definition of Risks, (2) Land Disposal, (3) International Approaches to and Issues Regarding Hazardous Waste Management, (4) New Technologies, (5) International Technological Advances, (6) Extractive Industries, (7) Thermal Destruction, (8) Waste Stabilization, (9) Nuclear Waste, (10) Chemical and Biological Treatment Processes, (11) State/Federal/Institutional Approaches to Hazardous Waste Management.

This proceedings is a compilation of speakers, papers or abstracts presented at the conference. The conference was sponsored by the U.S. Environmental Protection Agency, NUS Corporation, National Science Foundation, and the American Academy of Environmental Engineers.

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DEVELOPMENTS IN ASSESSING RISKS AT HAZARDOUS WASTE SITES

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ABSTRACT

A number of recent reports by EPA and other organizations document available techniques for assessing the risks associated with human exposure to toxic chemicals. These reports are intended to provide a conceptual framework for risk assessments both at the national level and in site-specific situations. They are very helpful in considering general toxicological, epidemiological, and exposure issues, but they provide very limited guidance for addressing the types of situations encountered at hazardous waste sites.

Data limitations severely reduce the usefulness of the formalized toxicity and exposure assessment procedures advocated in these reports. Consequently, the use of action levels expressed as concentration ranges of pollutants in soil and ground water and the use of comparisons of chemical concentrations in contaminated and control areas offer more practical approaches as a basis for action. A review of the risk assessment aspects of remedial action decisions at 30 Superfund sites highlights the difficulty in standardizing risk assessment procedures.

Trends in Chemical Risk Assessment

Recent studies by the National Academy of Sciences, the Office of Science and Technology Policy, and the National Science Foundation reflect the increasing sophistication that is being advocated for characterizing chemical risk assessments undertaken in support of regulatory activities (1,2,3). Perhaps of greater significance is the series of more detailed assessment guidelines for risk assessments published by EPA (4). Also of considerable importance are the many consent decrees and judicial decisions directed to reducing risks under a number of existing environmental statutes at both the Federal and State levels.

The strengths and weaknesses in using animal studies to predict health effects are better understood and more widely recognized than ever before. The toxicity differences

among isomers of the same chemicals are finally being acknowledged. The possibilities of chemical transformations of pollutants before and after they contact people are increasingly documented. At long last a common lexicon for frequently used terms is evolving. For example, "exposure" is now recognized to be the pollutant concentration at the body surface where chemical absorption may occur while "dose" is differentiated as the concentration in a critical organ or tissue (5). Finally, the concept of total integrated human exposure, including indoor exposure, is generally accepted as the basis for estimating likely health effects.

Still many aspects of risk assessment remain elusive. For example, the synergistic and antagonistic aspects of mixtures remain but vague concepts. The significance of high short-term exposures as

contrasted to low sustained exposures is not well understood. An inability to reconstruct historical exposures plagues litigation efforts. Perhaps most discouragingly even our best toxicity and exposure models can never be fully utilized given the shortage of sound data for such models.

Only in a very few cases can we be reasonably certain of the accuracy of risk assessments. The models being used are helpful in structuring analyses but rapidly give way to scientific and non-scientific judgments in providing definitive guidance on corrective actions.

Risk Assessment and Risk Management

For more than a decade there have been extensive efforts within and outside the Government to separate the scientific and policy aspects in determining regulatory responses to environmental risks. Most recently EPA has advocated two discrete decision processes -- risk assessment and risk management (6). While such a dual emphasis should help distinguish scientific facts from social and economic judgments, seldom is there a clear distinction between these two aspects.

A scientific consensus is lacking on many key points affecting risk calculations (7). The details of interpreting data from animal experiments, in particular, are a constant source of scientific disputes. Alternative techniques for extrapolating dose-response curves to low exposure levels, for example, can result in risk estimates varying by three orders of magnitude (8). Thus, the choice of the scientific technique is, in effect, a risk management decision. Similarly, selections of other controversial scientific approaches which are central to quanti-

tative risk assessment should be considered risk management decisions.

The establishment of an action level of 1 ppb for dioxin in soil, originally to be used at Times Beach and then used at many other sites, was clearly a risk management decision (9). Its portrayal as a scientific determination has been very misleading. There were many uncertainties in the calculations supporting this number, and other numbers also could have been generated from the same scientific data base. However, the most important aspect was the disregard of cost implications in setting this action level, since costs are at the very heart of risk management decision making.

Uncertainties in Risk Assessments

Environmental decision makers are usually reluctant to face up to the many uncertainties inherent in risk assessments. The lawyers warn that acknowledgements of such uncertainties can be used by opponents in efforts to overturn decisions. Perhaps more importantly, explicitly displaying uncertainties greatly complicates the value judgments that must be made.

Two of the most common and largest types of uncertainties are introduced in toxicological assessments. First, as noted above the type of dose-response extrapolation that is used dramatically influences the quantitative estimate. Secondly, safety factors are routinely used in such assessments, as indicated in Figure 1, and these factors are often referred to as uncertainty factors (10). These types of uncertainties usually reflect "orders of magnitude" uncertainties yet they are seldom highlighted in presenting what appear to be definitive quantitative estimates of risk.

- Use a 10-fold factor when extrapolating from studies on prolonged ingestion by man.
- Use a 100-fold factor when extrapolating from long-term feeding studies on experimental animals.
- Use a 1000-fold factor when extrapolating from less than chronic results in experimental animals.
- Use an additional factor of 1 to 10 when deriving an Allowable Daily Intake from a Lowest Observed Adverse Effect Level.

Figure 1. Guidelines for Use of Uncertainty (Safety) Factors (10).

With regard to exposure estimates, the greatest uncertainties are usually associated with population activity patterns since personal dosimetry programs for the general public do not exist. Activity pattern determinations on a retrospective or prospective basis are always very crude. Drinking water and dietary intake patterns are reasonably well known, but regulatory efforts seldom address other types of exposure with any degree of certainty.

Also frequently ignored are the difficulties in relating exposure to dose. The pharmacokinetic data for determining such relationships seldom exist.

The most highly publicized uncertainty estimates are those associated with environmental measurements, uncertainties which are almost always small in comparison to those described above. However, even with regard to measurement errors, the focus is frequently misdirected.

Usually, measurement errors center on errors introduced in the analytical laboratory, errors commonly in the range from 10 to 100 percent. Far larger errors can easily be introduced through inappropriate designs of sampling programs or faulty sampling and sample handling procedures.

The recent EPA guidelines on exposure assessment address some aspects of uncertainty in very general terms (11). While the statistical tests that are suggested to address limited numbers of samples, small affected populations, and sparse data for modelling efforts reflect long overdue attention to these problems, the guidance is of limited relevance to the practical problems of hazardous waste site assessment.

Action Levels for Soil and Ground Water

Previous studies have documented the inadequacy of the traditional approach of coupling estimates of human exposure to individual chemicals with laboratory studies of the toxicity of the chemicals as the basis for quantitative assessments of risk when considering problems near hazardous waste sites (12). The inevitable inadequacy of data and the uncertainties associated with the environmental behavior and effects of chemical mixtures and with containment are simply too large.

A review of 30 Superfund cleanup decisions underscores the need for programmatic and simple indicators of risk situations (13). In not one case was classical risk assessment feasible. Specifically, action levels for cleaning up soil and groundwater contamination are the key missing ingredients. However, in view of the enormous financial implications, in addition to the health and environmental aspects, these action levels must be carefully determined.

The methodology for establishing an action level of 1 ppb for dioxin in soil should not be repeated. Determination of an action level is a risk management decision. Therefore, an appropriate action level should vary from site to site, and generic action levels for individual chemicals should be expressed as action ranges. For example, the dioxin action range might more appropriately be .1 to 10 ppb depending on the type of soil which influences dose calculations, the location of the site, the likelihood of child exposure at the site, and the cost of cleanup.

With regard to ground-water contaminants which are already regulated under the Safe Drinking Water Act, ground-water action levels should probably not be the same as the drinking water standards. While the standards take into account "feasibility" considerations, they are based on the feasibility of operating a water supply system in a manner that will attain the prescribed levels. Ground-water cleanup is a different matter, and therefore, different feasibility criteria should obtain. Again an action range from a minimum level of the drinking water standard to a maximum level of perhaps an-order-of-magnitude higher might be appropriate. The level to be used in a particular case would be based on a site-specific risk management determination.

Monitoring Data and Risk Management Decisions

Since there is little likelihood that materials balances, pathway analysis, or modelling approaches will alone provide authoritative information concerning exposure levels near waste sites, monitoring data play a central role in risk management decisions. Such data are used in different ways -- for example, to determine contaminant levels of

individual chemicals or groups of chemicals as the basis for "absolute" risk judgements or to compare contaminant levels near sites with levels in control areas in determining "relative" risks.

Two types of "controls" seem appropriate. A control area with characteristics similar to the area of environmental concern is highly desirable. Of special interest would be a control area near the waste site -- but insulated by geographic features from the direct influence of the site. This area would be impacted by all of the industrial emissions and effluents that permeate the region as well as other common sources of contamination such as agricultural chemicals. Thus, in comparing the contamination near the site with the contamination in the control area, it should be possible to attribute any higher levels found near the site to the influence of the site itself and not to the background characteristics of the region. A second type of control can be provided by national or regional baseline data. Such data indicating the levels of ambient or background contamination usually encountered in different types of demographic settings can help clarify the significance of environmental measurements near a hazardous waste site.

Obviously, risk assessment data requirements should be a principal factor in investigating a waste site. A combination of assessing absolute risks associated with selected chemicals found near the site together with comparing general contamination near the site with contamination in control areas appears to be the most feasible approach. For large or complicated areas, the sampling plan should be tied to a geographic grid to facilitate analyses of all contributing sources and pathways.

Given the importance of monitoring data, care is needed in implementing monitoring programs. Figure 2 sets forth a general framework that should avoid many common pitfalls.

- Objectives must be defined by data users at outset.
- Program should be deliberately oriented to identifying hot-spots and/or assessing long-term habitability.
- All monitoring opportunities, and particularly pollutant pathways, should be examined at the outset.
- Statisticians and photo interpreters should assist in designing program.
- Before any sampling, an overall sampling plan should be developed with provisions for mid-course corrections.
- 20-30 percent of sampling should be for preliminary and confirmatory sampling.
- Sampling plan should explicitly address previous controversial findings.
- Alternative sampling sites should be pre-selected in event of access problems.
- Geophysical investigations can help target soil and groundwater sampling sites.
- Field and laboratory QA programs may account for 15 to 20 percent of monitoring costs.
- Sample holding times must be minimized.
- Since sample contamination is frequent, suspect data should be revalidated or discarded.
- Approach to data formatting and presentation should be jointly determined with data users.
- Data quality should be clearly differentiated from data interpretation.

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Disclaimer

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HAZARDOUS WASTE RISK ANALYSIS:
A NEW APPROACH BASED ON USER-INTERACTIVE ALGORITHMS

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ABSTRACT

The quantification and management of risk is very prominent among the new concepts in hazardous waste disposal. Risk quantification is an essential ingredient to wise, long-term waste management. New analytical techniques can now extract valuable information from an area that was once considered to be too elusive and subjective to measure. Once risks can be quantified, management techniques can be implemented to minimize unavoidable dangers, and to guarantee that risks are equally distributed.

In this paper we will describe a family of microcomputer-based, user-interactive risk analysis algorithms based on the Decision Alternative Ratio Evaluation (DARE) technique. It is demonstrated that when the required pairwise comparisons of technology alternatives are treated as known, a unique cardinal scale risk rating is produced. It is also demonstrated that the procedure may accommodate uncertainty to yield a probabilistic evaluation. All of the algorithms presented have been designed for implementation in a user-friendly programming style. Experience has shown that this helps to reduce user-intimidation and thereby enhances implementation. This allows users to come from a wide variety of backgrounds (e.g., the general public, engineers, environmentalists, politicians, industrial representatives etc.). Often, this can provide the positive, constructive involvement required for innovative waste management solutions.

INTRODUCTION

The analysis and control of risk is one of the most challenging problems of modern hazardous waste management. Our past experiences have dramatically illustrated the consequences of ignoring risk. Experience has also demonstrated that new waste management plans will not be successful (i.e. will not survive public inspection), unless the issues of risk are given serious attention. However, technological risks can be very difficult to assess given the vast mechanistic and operational differences between competing hazardous waste technologies. Risk analysis becomes even more elusive when one considers that it is often the "social perception" of these risks (rather than the

actual risks themselves) that constrain the possible outcomes.

In this paper, methods will be presented for quantifying the relative risks of alternative technologies. Although these may be used in detailed technical calculations to process site specific physical and chemical information, they also generalize to completely subjective "opinionated preference" analysis. Therefore, the methodology may be used to generate greater positive public involvement in the issue of risk management. With this particular application in mind, the algorithms presented here have been designed specifically for user-friendly, user-interactive microcomputer implementation.

PURPOSE

The risk analyses discussed here can best be appreciated in the context of the specific role they are intended to play in management planning. Jennings and Sholar(1) have recently demonstrated that the mathematical form of the "regional hazardous waste management problem" subsumes a transportation routing optimization. By this analogy, the "flow" of hazardous materials is treated as a constrained (forced) mass transfer through a network of generation sources, processing and storage nodes, and ultimate disposal sinks. This network concept is illustrated schematically in fig 1. Note that links do not necessarily imply significant distances. All network activities could (for example) occur on-site at a single industry. Obviously, the network could also model the aggregate management activities of a large region or state.

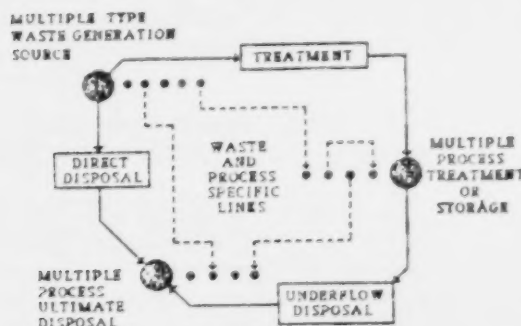


FIGURE 1- Schematic Flow Diagram of the Hazardous Waste Management Planning Network "Flow" Concept.

Disposal of hazardous materials requires the undesired movement of mass through this network (undesired in the sense that zero generation would be the ideal solution). Therefore, the problem must be cast in the form of a minimization to reduce the total undesired impact. It has also

been demonstrated (1) that these impacts may be expressed as any set of penalty functions defined on either the cost or risk of all network activities.

One of the substantial complications in this network approach is that, for general planning purposes, it is desirable to consider a wide variety of waste types and potential management technologies. This allows one to identify the most valuable treatment and disposal alternatives and to generate sound operating strategies before moving to detailed implementation planning. However, this requires that the potential network penalties (costs or risks) be evaluated for a wide variety of conditions. This is no easy task for either penalty, but the results of several recent studies are now available to provide guidelines for cost functions (2,3,4,5).

It is far more difficult to identify risk analysis procedures that are successful in crossing the conceptual barriers between distinct chemical waste types or disposal technologies. Procedures can be found (6,7,8,9) to rank (or rate) the dangers innate to specific chemical groups (i.e. chlorinated organics), or general process modifications (i.e. types of high temperature incineration). Few offer the flexibility required during framework planning stages.

The risk analysis procedures described here are intended to fill this void. They have been designed specifically to generate risk penalty functions for framework management planning. They yield cardinal scale risk ratings (in arbitrary units of relative risk) that preserve all the relative information of cost functions. These methods also acknowledge that risk analysis is innately less accurate than cost analysis. There-

fore, the procedures have been designed to account for uncertainty (imprecision) and also to yield information on the confidence that should be associated with any risk rating.

APPROACH

User-interactive methods to extract analysis information for risk have been constructed from modifications of the Decision Alternative Ratio Evaluation (DARE) algorithm of Klee(10). Both RISK1 (a deterministic model) and RISK2 involve a series of pairwise comparison of disposal alternatives against a set of potential consequences to human health and environment as the criteria. Klee(10) has also demonstrated how successive pairwise comparison of alternatives yields a cardinal scale of relative ratings while keeping the number of comparisons to a minimum.

Briefly, the DARE algorithm can be characterized by the following 4 steps:

STEP 1: Selection of M potential consequences as the criteria for which the alternative technologies are to be evaluated.

STEP 2: Assigning weights for each of the M criteria to specify their relative importance to the overall analysis. These weights may be arbitrarily assigned or computed by a DARE analysis of potential consequences.

STEP 3: Selection of N hazardous waste management alternatives to be rated.

STEP 4: Conduction of (N-1) pairwise comparisons of the N management technologies (for each of the M consequences) to construct a preference heirarchy.

Steps 2 and/or 4 may be treated as being precise (deterministic) or imprecise due to user uncertainty or imprecision.

1. THE DETERMINISTIC APPROACH:

The mathematical formulation to yield a deterministic, cardinal scale risk rating is as follows:

Let W be a $M \times 1$ constrained vector containing the weights of the M selected consequences such that $\sum W_j = 1.0$. Let U be a $N \times M$ matrix storing the user-supplied evaluations such that:

$$U_{Nj} = 1.0 \quad \forall j=1, M$$

$$U_{ij} \neq 0.0 \quad \forall i=1, N-1; j=1, M.$$

A risk heirarchy matrix H may then be computed as follows:

$$H_{ij} = \sum_{k=i}^N U_{kj} \quad \forall i=1, N; j=1, M.$$

H may then be normalized to yield the final rating matrix F .

$$F_{ij} = \frac{H_{ij}}{\sum_i H_{ij}} \quad \forall i=1, N; j=1, M$$

The final cardinal scale risk rating for each alternative may then be computed from H and the weight vector W .

$$R_i = \sum_{j=1}^M F_{ij} W_j \quad \forall i=1, N$$

2. THE STOCHASTIC APPROACH:

The fundamental techniques involved in this approach are similar to those described above. However, one or more quantities in this analysis are considered to be fuzzy. This leads to a more complicated problem structure because a distribution of values must now replace

what had earlier been single-valued elements. To resolve this problem, one must select possible values from each distribution such that they result in the true upper and lower bounds for the risk values. By assigning a probability to this selection, bounds can be calculated for different levels of confidence. This procedure is defined as follows:

Let $\tilde{W}$ be a $M \times 1$ vector containing fuzzy weights of the M potential consequences such that

$$\tilde{W}_{jmin} \leq \tilde{W}_j \leq \tilde{W}_{jmax} \quad \forall j=1, M.$$

One must also impose the constraint that

$$\sum_{j=1}^M \tilde{W}_j = 1.0.$$

It is also necessary to prescribe a distribution for $\tilde{W}_j$ values between

$\tilde{W}_{jmin}$ and $\tilde{W}_{jmax}$. For this work, it

has been assumed that these are normally distributed, and contain the true value of $\tilde{W}_j$ with a probability of 0.99.

Now let $\tilde{U}$ be a $(N \times M)$ matrix of user supplied evaluations (Similar to the deterministic approach).

$$\tilde{U}_{Nj} = 1.0 \quad \forall j=1, M$$

$$\tilde{U}_{ij} \neq 0.0 \quad \forall i=1, N-1; j=1, M$$

Elements of $\tilde{U}$ may now be any number contained by known bounds.

$$\tilde{U}_{ijmin} \leq \tilde{U}_{ij} \leq \tilde{U}_{ijmax}$$

$$\forall i=1, N-1; j=1, M$$

Let $\tilde{F}$ be a $N \times M$ matrix of final normalized risk evaluations. The problem may now be solved by picking those

values of $\tilde{U}_{ij}$ for each alternative that result in the upper and lower bounds of $\tilde{F}_{ij}$.

The selection procedure for $\tilde{U}_{ij}$ values is as follows.

To obtain $\tilde{F}_{ijmax}$, select (for all $i=1, N$)

$$\tilde{U}_{ij} = \begin{cases} \tilde{U}_{kjmax} & \forall k=i, N; j=1, M \\ \tilde{U}_{kjmin} & \forall k=1, i-1; j=1, M. \end{cases}$$

To obtain $\tilde{F}_{ijmin}$, select (for all $i=1, N$)

$$\tilde{U}_{ij} = \begin{cases} \tilde{U}_{kjmin} & \forall k=i, N; j=1, M \\ \tilde{U}_{kjmax} & \forall k=1, i-1; j=1, M. \end{cases}$$

Using these values of $\tilde{U}_{ij}$, the risk heirarchy matrix $\tilde{H}$ may be computed as before.

$$\tilde{H}_{ij} = \prod_{k=i}^N \tilde{U}_{kj} \quad \forall i=1, N-1; j=1, M$$

It should be noted that this risk heirarchy matrix must now be calculated twice (once to calculate $\tilde{F}_{ijmax}$ and once to calculate $\tilde{F}_{ijmin}$).

The values of these extremes are computed using the corresponding risk heirarchy values:

$$\tilde{F}_{ij} = \frac{\tilde{H}_{ij}}{\sum \tilde{H}_{ij}} \quad \forall i=1, N; j=1, M.$$

The structure of $\tilde{F}$ and $\tilde{W}$ are illustrated in figure 2.

The final cardinal scale risk rating R_i for each alternative can then be obtained (as before) using the relation:

$$R_i = \sum_{j=1}^M \tilde{F}_{ij} \tilde{W}_j \quad \forall i=1, N.$$

TECHNOLOGY ALTERNATIVE	POTENTIAL CONSEQUENCE					
	I		J		M	
1	$f_{11min} \leq f_{11}$ $f_{11} \leq f_{11max}$	..	$f_{1jmin} \leq f_{1j}$ $f_{1j} \leq f_{1jmax}$	..	$f_{1Mmin} \leq f_{1M}$ $f_{1M} \leq f_{1Mmax}$	
2	$f_{21min} \leq f_{21}$ $f_{21} \leq f_{21max}$	..	$f_{2jmin} \leq f_{2j}$ $f_{2j} \leq f_{2jmax}$	..	$f_{2Mmin} \leq f_{2M}$ $f_{2M} \leq f_{2Mmax}$	
:	:		:		:	
i	$f_{i1min} \leq f_{i1}$ $f_{i1} \leq f_{i1max}$	..	$f_{ijmin} \leq f_{ij}$ $f_{ij} \leq f_{ijmax}$	..	$f_{iMmin} \leq f_{iM}$ $f_{iM} \leq f_{iMmax}$	
:	:		:		:	
N	$f_{N1min} \leq f_{N1}$ $f_{N1} \leq f_{N1max}$	..	$f_{Njmin} \leq f_{Nj}$ $f_{Nj} \leq f_{Njmax}$	..	$f_{NMmin} \leq f_{NM}$ $f_{NM} \leq f_{NMmax}$	

POTENTIAL CONSEQUENCE	WEIGHT	
1	$w_{1min} \leq w_1$ $w_1 \leq w_{1max}$	
2	$w_{2min} \leq w_2$ $w_2 \leq w_{2max}$	
:	:	
j	$w_{jmin} \leq w_j$ $w_j \leq w_{jmax}$	
:	:	
M	$w_{Mmin} \leq w_M$ $w_M \leq w_{Mmax}$	

FIGURE 2 - Structure of the fuzzy matrices $\tilde{F}$ and $\tilde{W}$

In this case however, one must calculate the upper and lower bounds for R_i using combinations of upper and lower bounds from F_{ij} and W_j .

At a first glance it would appear that using all upper bounds of W_j and F_{ij} would yield an upper bound on R_i while using lower

bounds would yield the lower bound. However, closer scrutiny reveals that in such a case the weight constraint $\sum W_j = 1.0$ would be violated.

Therefore, in order to select the combination of weights to yield the true upper and lower bound on R_i while satisfying the weight constraint, the following procedure is proposed.

Let $\tilde{F}(C, \max)_i^T$ and $\tilde{F}(C, \min)_i^T$ be

vectors of extreme $\tilde{F}$ values for the i th management alternative written in decreasing order of magnitude for a specified degree of confidence (C). Let

$\tilde{W}(\max)_i$ and $\tilde{W}(\min)_i$ be the appro-

priately reordered vectors of minimum weights for this same degree of confidence. Also, let us define:

$$\Delta W_j = \{W_j(\max) - W_j(\min)\} \quad \forall j=1, M$$

$$Rem(\max) = \sum_j W_j(\max) - 1.0$$

$$Rem(\min) = 1.0 - \sum_j W_j(\min).$$

The elements of $\Delta \tilde{W}$ must also be

reordered to yield $\Delta \tilde{W}(\max)_i$ and

$\Delta \tilde{W}(\min)_i$. Given these, the extreme rankings may be computed as follows:

$$R_i(\max) = \{\tilde{F}(C, \max)_i^T [\tilde{W}(\max)_i + \tilde{W}(\max)_{ii}]\} \quad \forall i=1, N$$

$$R_i(\min) = \{\tilde{F}(C, \min)_i^T [\tilde{W}(\min)_i + \tilde{W}(\min)_{ii}]\} \quad \forall i=1, N$$

where: $\tilde{W}(\max)_{ii}$ is obtained as follows.

$$Rem_1 = Rem(max)$$

$$Rem_j \geq \Delta \tilde{W}_j(max)_i \Rightarrow \tilde{W}_j(max)_{ii} = \Delta \tilde{W}_j(max)_i$$

$$Rem_j < \Delta \tilde{W}_j(max)_i \Rightarrow \tilde{W}_j(max)_{ii} = Rem_j$$

$$Rem_{j+1} = Rem_j - \tilde{W}_j(max)_{ii}$$

$$Rem_{j+1} < 0.0 \Rightarrow \tilde{W}_j(max)_{ii} = 0.0$$

$$\forall i=1,N; j=1,M$$

Next, $\tilde{W}(min)_{ii}$ is obtained as follows:

$$Rem_M = Rem(min)$$

$$Rem_k \geq \Delta \tilde{W}(min)_i \Rightarrow \tilde{W}_k(min)_{ii} = \Delta \tilde{W}_k(min)_i$$

$$Rem_k < \Delta \tilde{W}_k(min)_i \Rightarrow \tilde{W}_k(min)_{ii} = Rem_k$$

$$Rem_{k-1} = Rem_k - \tilde{W}_k(min)_{ii}$$

$$Rem_{k-1} < 0.0 \Rightarrow \tilde{W}_k(min)_{ii} = 0.0$$

$$\forall k=M,1; i=1,N.$$

This represents the completion of one pass of the algorithm. The first pass values are assumed to represent the 99% confidence limits. Additional confidence interval results are produced by reducing the bounds on the weight and rating values to represent different degrees of confidence.

MICROCOMPUTER IMPLEMENTATION

The algorithm described above has been programmed in FORTRAN 77 for the IBM Personal Computer. The program's user-friendly nature provides a non-intimidating atmosphere for even a first-time user. It also helps any user to implement what can be a tedious series of calculations.

The session starts with the user selecting the potential consequences to be considered in the analysis. This may be accomplished simply by making selections from the program's internal menu or by adding user-defined consequences. Consequence weighting is then accomplished by either simply assigning weights or by conducting a DARE analysis on the consequences themselves.

The next major step is to select waste treatment/disposal alternatives to be rated. Here again the user is encouraged to select from the program's internal menu. The user may also add management alternatives. The user is then required to rate the alternatives (taken in pairs) against all the consequences considered.

The program has been designed to instruct the user at every step in the session. It has also been protected (by internal logic) from non-sequitur input. At the end of the analysis session, an option is available for conducting a consistency check by re-ordering all the alternatives and repeating the rating process.

Results are printed out at each strategic point in the session. A typical risk analysis session would last about 15-30 minutes depending on user familiarity with the program. Currently, efforts are being made to add an on-line tutorial session to increase user awareness of process operating modes and potential failure scenarios.

The RISK2 source code requires about 40K bytes of memory. The executable form occupies about 95K bytes. Results of an example risk analysis session are presented below.

RUN TITLE: EXAMPLE RUN

A SUMMARY OF THE POTENTIAL CONSEQUENCES
SELECTED IS AS FOLLOWS:

5 CONSEQUENCES WERE SELECTED FROM THE INTERNAL MENU.
0 CONSEQUENCES WERE ADDED BY THE USER.

NO.	POTENTIAL CONSEQUENCES SELECTED
1	SITE WORKER OCCUPATIONAL HAZARD
2	OFF-SITE ACUTE HUMAN HEALTH HAZARD
3	OFF-SITE CHRONIC HUMAN HEALTH HAZARD
4	ACUTE ENVIRONMENTAL DAMAGE POTENTIAL
5	CHRONIC ENVIRONMENTAL DAMAGE POTENTIAL

A SUMMARY OF THE WEIGHTING FACTORS FOR THE
CONSEQUENCES IS AS FOLLOWS:

CONSEQUENCE NO.	WEIGHT		
	LOWER BOUND	MEAN	UPPER BOUND
1	.142500	.150000	.157500
2	.180000	.200000	.220000
3	.291000	.300000	.309000
4	.170000	.200000	.230000
5	.142500	.150000	.157500

A SUMMARY OF THE TREATMENT/DISPOSAL ALTERNATIVE
SELECTION IS AS FOLLOWS:

7 ALTERNATIVES WERE SELECTED FROM THE INTERNAL MENU.
0 ALTERNATIVES WERE ADDED BY THE USER.

NO.	TREATMENT/DISPOSAL MANAGEMENT ALTERNATIVE
1	ROTARY KILN INCINERATION
2	LIQUID INJECTION INCINERATION
3	OCEAN INCINERATION
4	SECURE LANDFILL
5	LAND TREATMENT
6	DEEP WELL INJECTION
7	SOLVENT RECOVERY BY REDISTILLATION

A SUMMARY OF THE USER SUPPLIED PAIRWISE RISK
EVALUATIONS IS AS FOLLOWS:

MANAGEMENT OPTION NO.	CONSEQUENCE INDEX NUMBER				
	1	2	3	4	5
1	.85	1.00	1.00	.90	1.00
2	.60	.80	1.00	.85	1.00
3	1.35	1.20	.30	1.50	.50
4	.70	.80	.40	1.00	.70
5	1.20	1.50	1.00	1.00	1.00
6	.50	.50	2.00	1.00	2.50
7	.00	.00	.00	.00	.00

THE FINAL RESULTS OF YOUR RISK ANALYSIS ARE AS FOLLOWS:

THESE RESULTS INDICATE THE LOWER AND UPPER BOUNDS
PREDICTED FOR THE RISK VALUES WITH 99% CONFIDENCE.

MANAGEMENT OPTION NO.	RISK VALUES	
	LOWER BOUND	UPPER BOUND
1	.063	.119
2	.072	.119
3	.093	.139
4	.114	.148
5	.187	.234
6	.172	.222
7	.136	.209

THESE RESULTS INDICATE THE LOWER AND UPPER BOUNDS
PREDICTED FOR THE RISK VALUES WITH 95% CONFIDENCE.

MANAGEMENT OPTION NO.	RISK VALUES	
	LOWER BOUND	UPPER BOUND
1	.074	.135
2	.081	.107
3	.102	.128
4	.121	.139
5	.197	.223
6	.181	.209
7	.149	.190

THESE RESULTS INDICATE THE LOWER AND UPPER BOUNDS
PREDICTED FOR THE RISK VALUES WITH 50% CONFIDENCE.

MANAGEMENT OPTION NO.	RISK VALUES	
	LOWER BOUND	UPPER BOUND
1	.083	.094
2	.090	.099
3	.111	.119
4	.127	.133
5	.205	.214
6	.190	.200
7	.162	.176

THESE RESULTS INDICATE THE LOWER AND UPPER BOUNDS
PREDICTED FOR THE RISK VALUES WITH 0% CONFIDENCE.

MANAGEMENT OPTION NO.	RISK VALUES	
	LOWER BOUND	UPPER BOUND
1	.089	.089
2	.094	.094
3	.115	.115
4	.130	.130
5	.209	.209
6	.195	.195
7	.168	.168

SUMMARY AND CONCLUSIONS

The problem of effective management of hazardous wastes can be expressed conveniently as a transportation "routing" optimization problem. However, the penalty functions associated with the minimization problem are difficult to evaluate in terms of intangibles like risk. Public participation in such an evaluation is recognized to be extremely important if management programs are to be successfully implemented. Therefore, a risk analysis procedure (based on microcomputer technology) has been developed. This is designed to extract quantitative risk "opinion" information from the wide spectrum of people who must cooperate in a hazardous waste problem solution.

The information generated from these analyses can also be used in determining the uniqueness of risk values for a particular alternative. This can help define the most desirable hazardous waste management plan; one which is acceptable from a technical viewpoint while satisfying constraints on actual and public opinion of the levels of risk.

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SUBSURFACE ENVIRONMENTAL EMERGENCIES:
MANAGERIAL REQUIREMENTS FOR EXCELLENCE

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ABSTRACT

A subsurface environmental emergency such as an underground tank leak, an underground pipeline leak or an infiltrating chemical surface spill can be an incident of grave concern for industrial or governmental facility managers. No longer is the old cliché "out of sight; out of mind" acceptable. A subsurface environmental emergency (SEE) requires managers to literally "see" below the ground surface into what is to many managers, as well as their corporate or command supervisors, a mysterious environment.

The first managerial problem during a SEE is to provide the proper response. Solutions to this problem rest in a manager's knowledge of the specific subsurface problem and who can best respond to solve the problem. With today's technology, solving an acute ground-water contamination problem can be as quickly accomplished as solving an acute surface water contamination problem. Therefore the managerial requirements are to provide excellence in responding to site-specific hydrogeologic conditions and excellence in ground-water contamination identification and remediation.

The other managerial problem during a SEE is to provide satisfactory performance. Solutions rest in a manager's knowledge of the specifics for a SEE investigation. Satisfactory performance deals not only with how an investigation is accomplished, but also with the cost-effectiveness of the investigation techniques. Investigation methodologies such as employee interviews, review of site history, immediately available data acquisition, and use of appropriate investigation techniques are essential for a manager to understand. A manager should also understand the cost-effectiveness of one technique versus another. An example would be how cost-effective a remote sensing technique might be versus an exploratory drilling program. Therefore a manager must assure not only excellence in investigative methodology and data acquisition techniques but also in controlling expenditures.

An essential part of the successful performance of a task is assuring that an understandable report is prepared which results in corporate or command acceptance of the report. A report should address the critical items of the SEE in the proper perspectives.

This paper presents managerial requirements for excellence during a subsurface environmental emergency. Since a SEE response requires a timely reaction, prior knowledge of methodologies and techniques and a standard operating protocol are essential for managerial excellence. This paper specifically outlines for the manager procedures for SEE responses, performance and reporting. In addition specific examples of excellence in understanding subsurface and contaminant migration characteristics are cited.

INTRODUCTION AND PURPOSE

A subsurface environmental emergency such as an underground tank leak, an underground pipeline leak or an infiltrating chemical surface spill can be an incident of grave concern for industrial or governmental facility managers. A subsurface environmental emergency (SEE) requires managers to literally "see" below the ground surface into what is to many managers as well as their corporate or command supervisors a mysterious environment. Since a SEE response requires a timely reaction, prior knowledge of methodologies and techniques and a standard operating procedure are essential for managerial excellence. The purpose of this paper is to outline for the manager procedures for a SEE response, performance and report. The generalized procedural outline discussion is followed by a discussion of specific examples of problems and solutions in understanding subsurface and contaminant migration characteristics.

GENERALIZED PROCEDURAL OUTLINE

As a facility manager plans his or her program dealing with subsurface environmental emergencies, there are three major areas with which the manager should be concerned. These three

areas are the response to the SEE, the performance of the SEE investigation and the report following the SEE. The managerial requirements for excellence begin with the necessity to plan ahead in establishing a standard operating procedure (SOP) for subsurface environmental emergencies. For best results an SOP is essential during each of the three areas of concern.

The critical elements which should be addressed within an SOP for a SEE response are:

Facility

- Waste Handling and/or Storage Areas
- Petroleum, Oils & Lubricants (POL) Areas
- Underground Utilities

Federal Regulations

- Resource Conservation & Recovery Act
- Toxic Substances Control Act
- Conservation and Environmental Resource Control & Liability Act
- Safe Water Drinking Act
- Leaking Underground Storage Tank Regulations (Proposed)

State Environmental Regulations

Local Environmental
Regulations

Geological Characteristics
Regional
Vicinity
Facility
Ground-water Characteristics
Regional
Vicinity
Facility

Investigation Methodologies
General Knowledge
Availability of Specialists
Specialists in Specific
Fields
Geology
Ground Water
Geophysics
Remedial Actions

Response Time

Public Relations

Corporate or Command
Involvement

The critical elements which
should be addressed within an SOP
for the performance of the SEE
investigation are:

Timely Reaction
Mobilization
Efficiency
Daily Reports

Employee Interviews
Insights to Cause and
Effect Relationships
Potential Sources of SEE
Confirming Data

Facility History
Past Activities
Past and Present Activity
Relationships
Land Use Characteristics

Analysis of Available Data

Investigation Methodologies
Specific Techniques
Applicability
Confidence in Technique
Confidence in
Specialist
Assurance of Performance
Cost Effectiveness
Budget

The critical elements which
should be addressed within an SOP
for a SEE report are:

Interim Reports
Daily
Constant Re-evaluation
Recommendations

Draft Report
Concise
Executive Summary for
Corporate or Command
Reviewers
Specifics for Regulatory
Reviewers
Recommendations

Final Report
Appropriate Perspectives
Precise
Inclusion of Unanswered
Questions
Recommendations

SPECIFIC EXAMPLES

Environmental Consultants

Within above generalized out-
line a manager will probably have
the most problems with geological
and ground-water characteristics
as well as investigative methodol-
ogies. Geological and ground-
water characteristics can normally
be understood by reviewing

federal, state and local hydrogeological reports. Investigative methodologies are generally described in appropriate textbooks and professional journals, but the application of these methods may or may not be effective in all facility SEE investigations. For a manager to effectively manage a SEE investigation the manager should consult professionals in specific fields of interest. These may include -

- Hydrogeology
- Geophysics
- Monitoring Well Drilling
- Remedial Actions

A consultant which offers services in all of the above professions may be the most cost-effective for the facility manager. Then a problem arises when the manager learns that many consultants offer all of these services. The managerial requirement for excellence then becomes one not only of judgements of investigative methodologies but also and perhaps more importantly one of judgements of individuals. Individuals comprise a consulting company and individuals will perform the investigation at the facility. Therefore, knowing the most about individuals and their application of professionalism and investigative methodologies offers the facility manager the highest degree of excellence in the response, performance and reporting of a particular SEE. Knowledge about individuals can be obtained by evaluating:

- Resumes

- Professional Affiliations

Meetings

- First Impressions
- In-Depth Conversations
- Senario Presentations

References

- Personal
- Previous Day-to-Day
- Contacts with Other
- Facility Managers

Electrical Resistivity

Electrical resistivity (ER) is one of the most cost-effective investigative methodologies that can be applied during a SEE. One technique of ER which has proven to be very helpful and quite revealing in SEE investigations is the "Modified Wenner Array." Figure 1 illustrates the metal probe or electrode set-up in this array. An electrical current from batteries is conducted through the ground via the outer probes and the resulting voltage potential is measured via the inner probes. In the "modified Wenner Array" the inner probe distance across the ground surface has been found to be very close to the depth of investigation below the ground. Therefore, a manager may "see" within the subsurface through the eyes, experience and knowledge of a trained user of ER. Figures 2 and 3 are two examples of how well ER corresponds to actual subsurface conditions. Note how in Figure 2 the ER interpretation of the depth to the top of consolidated rock is similar to the actual depth.

In Figure 3 note how the sand zone between 52 and 58 feet is depicted by ER and how similar the ER and actual top of rock depths

are illustrated. The cost-effectiveness of ER can be realized by the proper application of ER to specific hydrogeological conditions. An exploratory drilling program designed to gather the same amount of subsurface data would be far more expensive than properly interpreting many ER measurements with only a minimum number of test borings.

ER can be used to detect ground-water contamination as well as to depict hydrogeological conditions. Figures 4 and 5 are two examples of how ER can be used to detect ground-water contamination. Figure 4 illustrates the detection of a localized area of contamination where as Figure 5 illustrates the detection of ground-water contamination over a broad area.

Monitoring Well Construction

Within the performance of a SEE investigation monitoring wells will more than likely be needed. Wells should be located upgradient and downgradient of the suspected source of contamination. As stated earlier ER is an excellent technique to utilize in the placement of select monitoring wells. Placement of wells as well as their construction are very critical elements in a SEE investigation. The design requirements of a well are factors such as -

- Drilling Logs
- Hydrogeological
- Classifications
- of Strata
- Well Materials
- Seals

The above factors are illustrated in Figure 6. A well written drilling log is simple to understand and easy to visualize. The hydrogeological classifications are normally straight-forward as seen in Figure 6. Well materials are based on the contaminant characteristics and the depth of the well. In the illustrated case, metal contamination in the confined aquifer was of concern. Polyvinyl chloride casing and screen was selected because organics were not of concern; four-inch diameter was selected because of its ease of development and because the client preferred to use a submersible pump for purging and sampling. Well seals of bentonite, cement grout and a locking cap insure the integrity of the well.

CONCLUSION AND SUMMARY

Subsurface Environmental Emergencies are of grave concern to industrial and governmental facility managers. Managers must "see" below their facilities into the subsurface to insure excellence in responding, performing and reporting of subsurface problems. Numerous factors may contribute to the effectiveness of a SEE investigation, but very few are effective without prior planning and an established standard operating protocol.

The two most important requirements for a manager to meet during a SEE are (1) to understand those who respond, perform and report to him or her and (2) to realize that cost-effective techniques such as electrical resistivity can be applied to yield critical data in the highest

expectations of investigative excellence.

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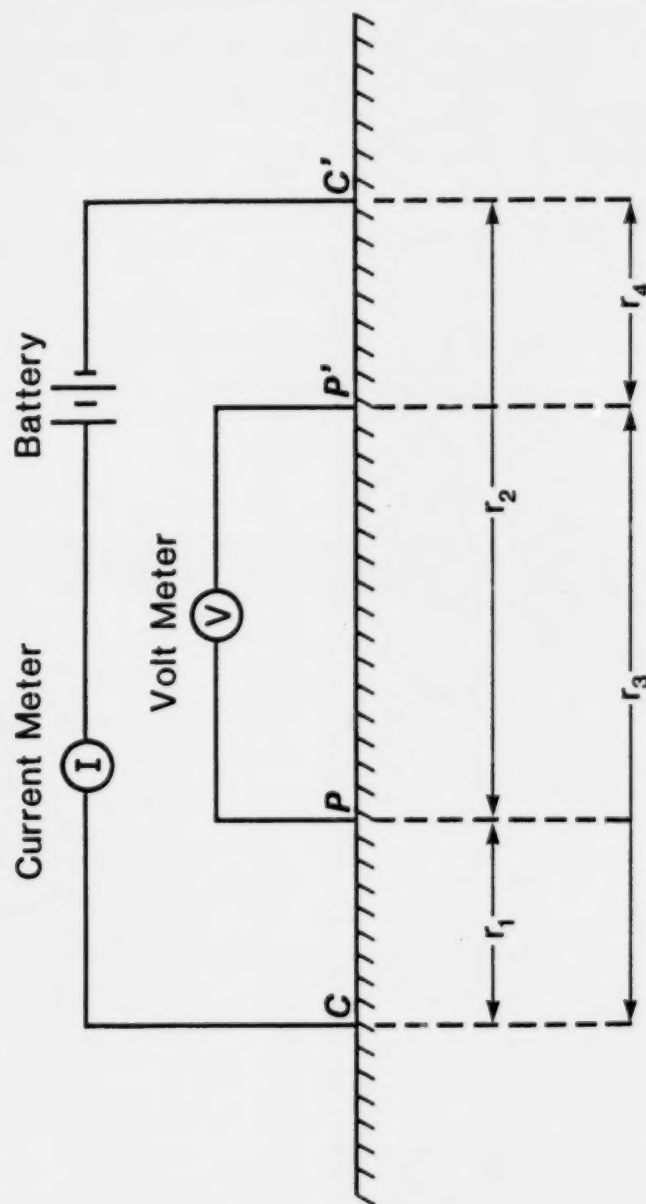
Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

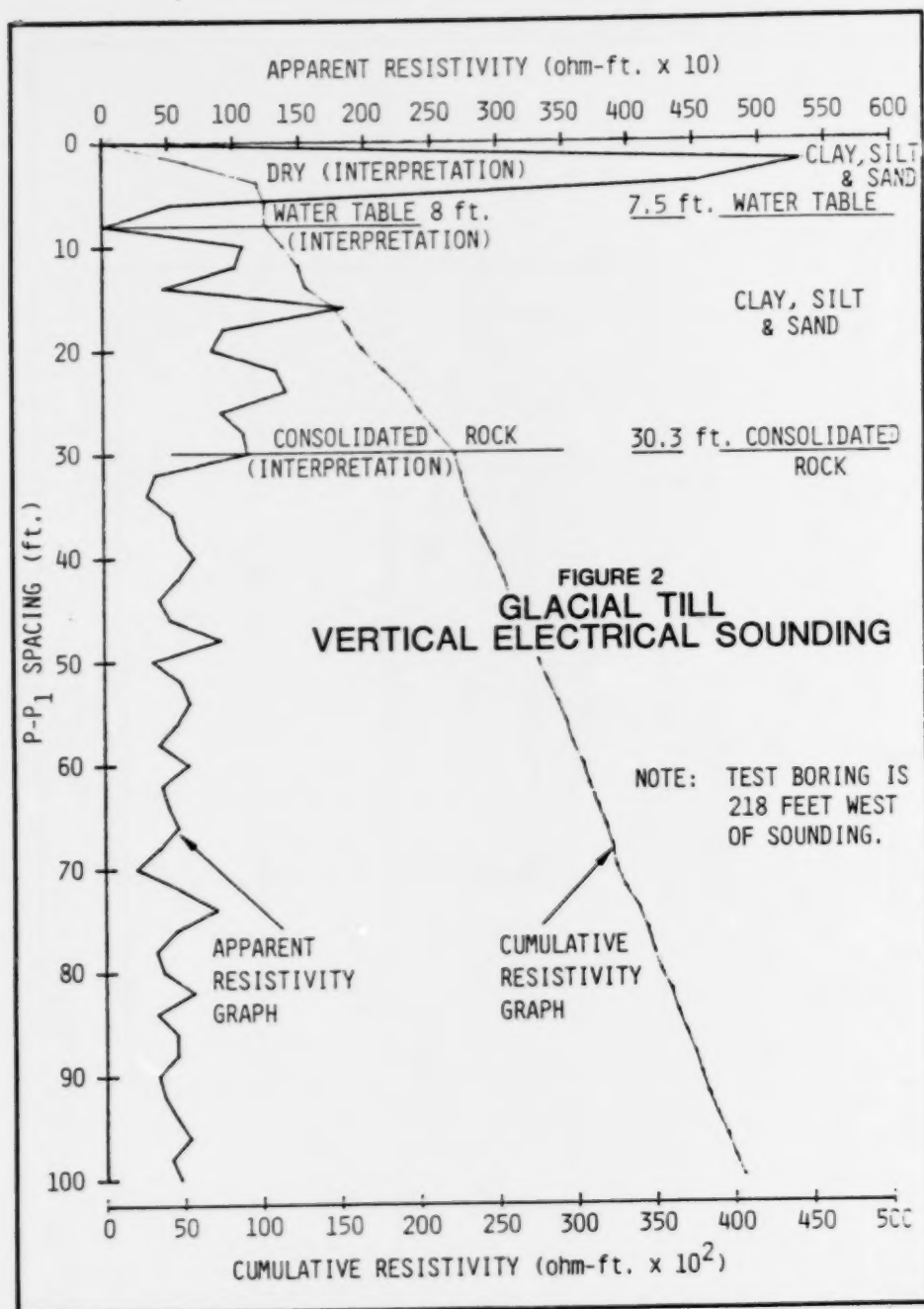
Formula for Apparent Resistivity

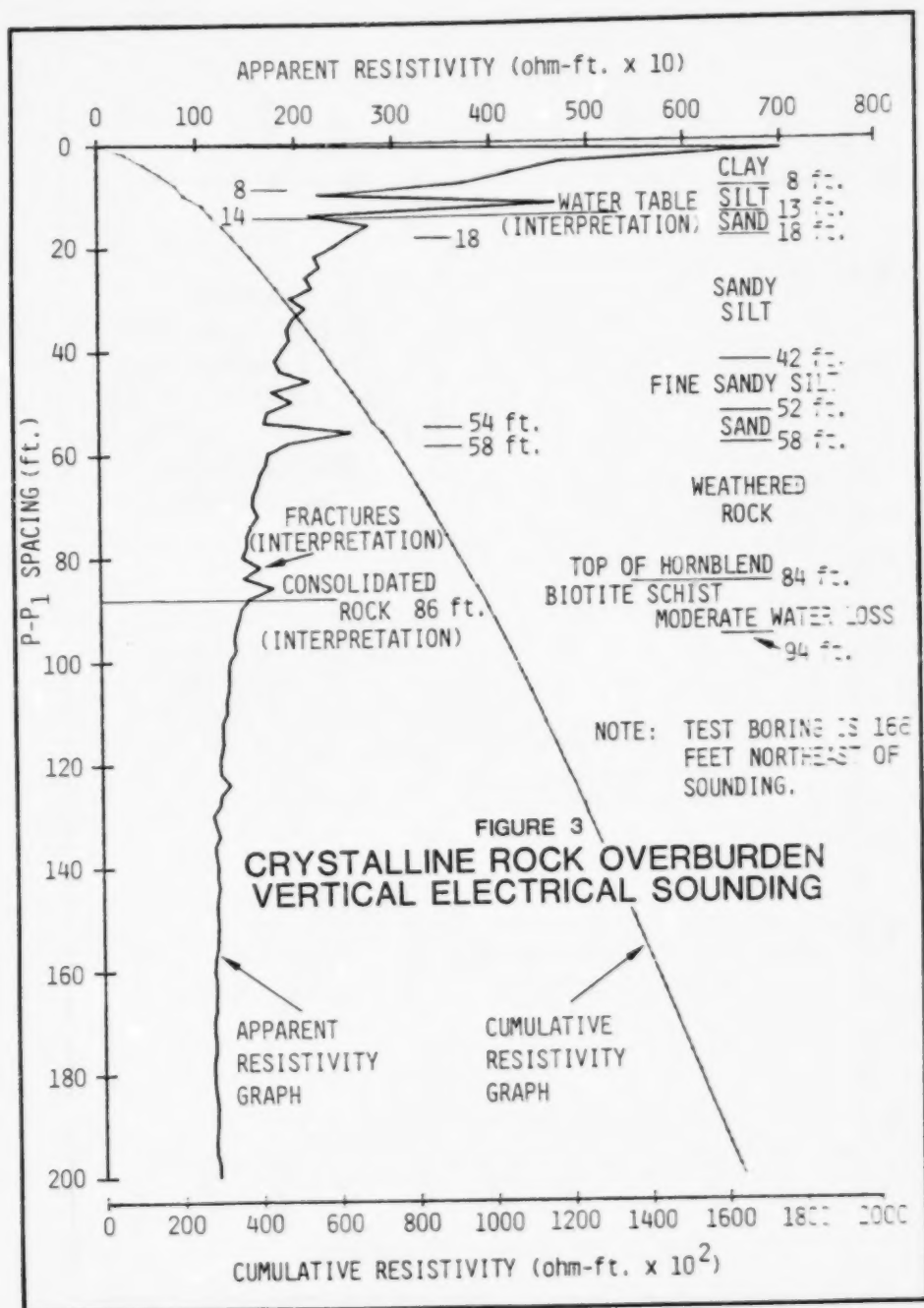
$$\rho = (2\pi R) \left[\frac{1}{\frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{r_3} + \frac{1}{r_4}} \right]$$

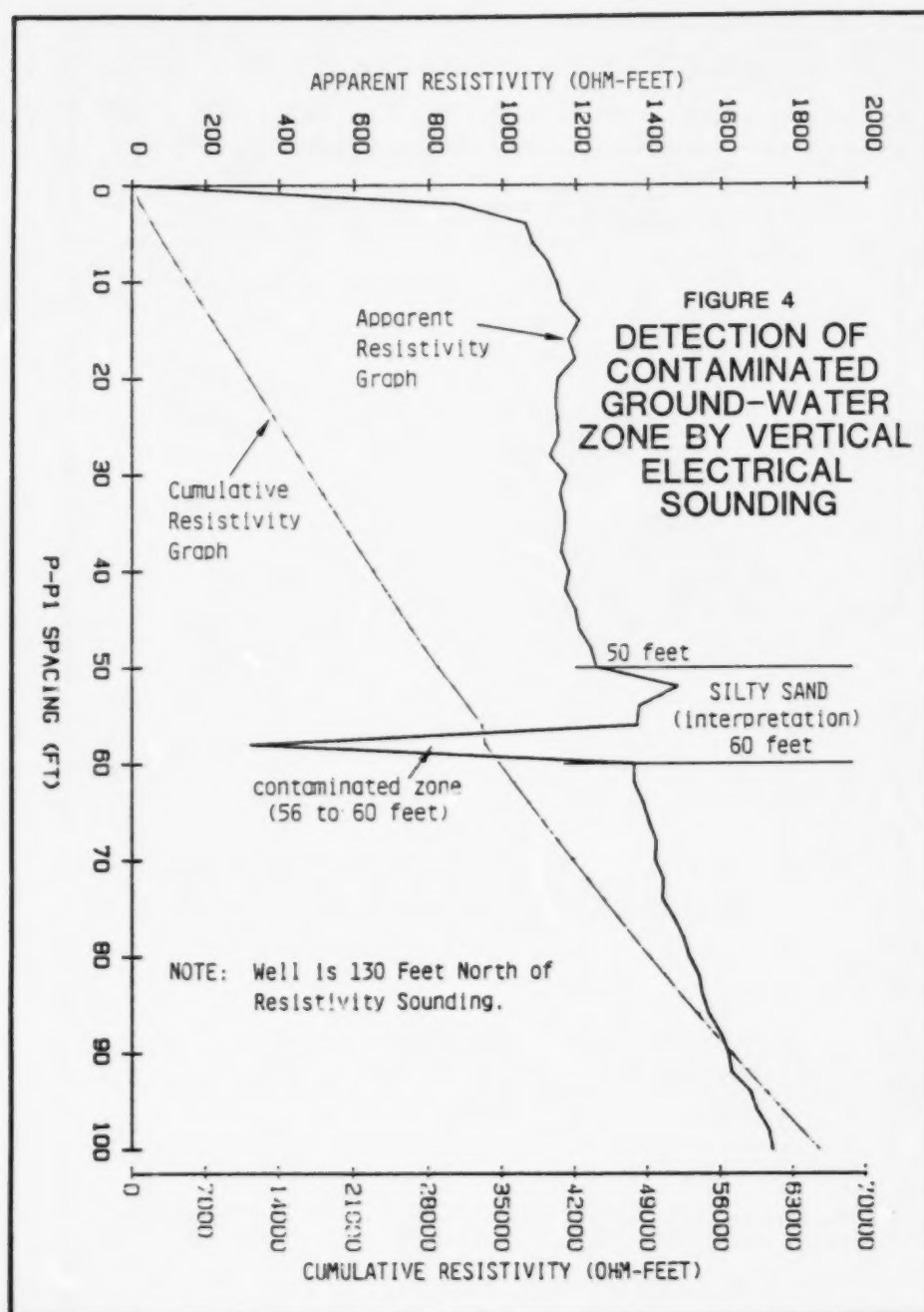
FIGURE 1
"MODIFIED WENNER" ARRAY
DIAGRAM OF ELECTRODE SPACING



SOURCE: Carrington & Watson, 1981







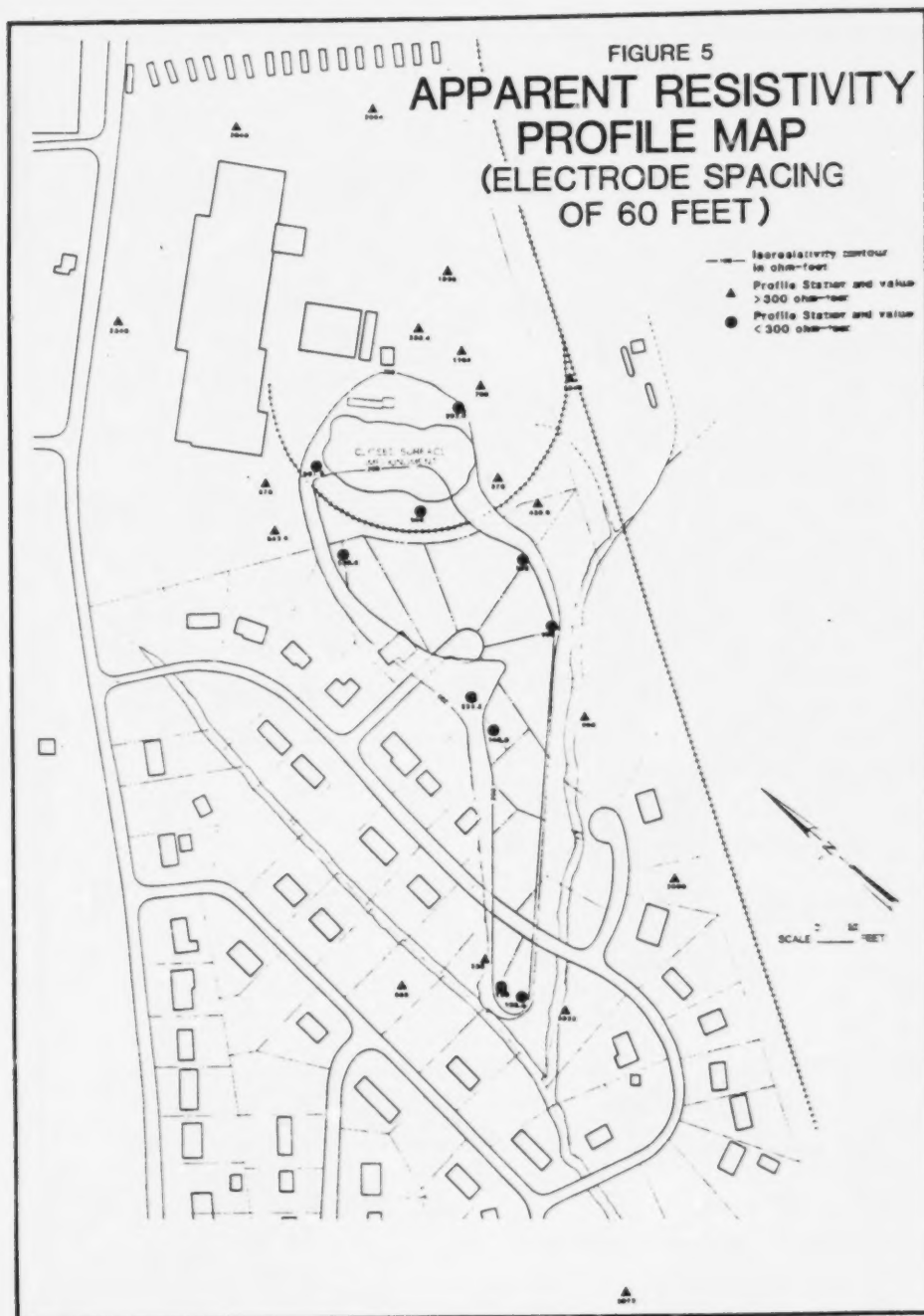
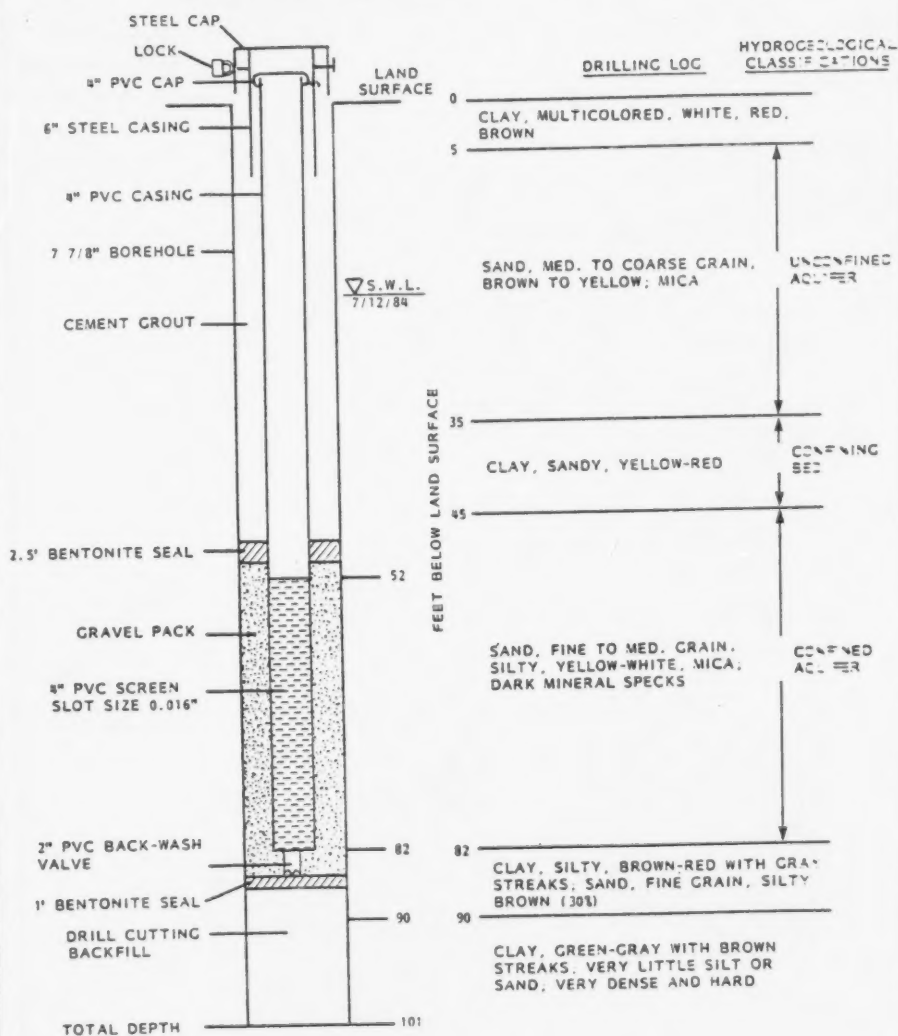


FIGURE 6
TYPICAL
MONITORING WELL CONSTRUCTION



RESTRICTIONS FOR LAND DISPOSED WASTES:
CAN THE INDUSTRY READILY COMPLY?

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ABSTRACT

Congressional legislation now mandates the restriction of certain hazardous wastes from land disposal. Although government officials and the public have assumed that such restrictions can be implemented, the capability for rapid implementation has not been evaluated. According to EPA data, most of the annual volume of hazardous waste generated already receives some treatment. Only 20 percent of this annual volume is disposed in the land and very little actually is placed in landfills (only 1 percent of the total volume). Current commercial capacity is limited, representing only one percent of the total unused capacity throughout the country.

A broad range of technologies exist now that can completely destroy or, at least, reduce hazards associated with industrial wastes. New technological developments make it possible to treat effectively mixtures of organic and inorganic wastes and to degrade previously recalcitrant constituents. Rapid commercial development of these alternatives to land disposal, however, is hampered by certain barriers. Currently, there is considerable difficulty in siting new treatment facilities. Regulatory standards are not available by which the effectiveness and efficiencies of new developments can be evaluated. As the goal of waste minimization is achieved, there will be uncertainties in the size and composition of future markets. Finally, the current pace and priorities of the federal and state permitting process delays expeditious commercial development. Until more efficient institutional mechanisms are developed to reduce these barriers, commercial capacities to manage land-restricted wastes may not be sufficient.

INTRODUCTION

The goal of the federal hazardous waste management program is to reduce dependence on land disposal as a predominant management option. Thus, the Hazardous and Solid Waste Amendments (HSWA) of 1984 include the mandate that the U.S. Environmental Protection Agency (EPA) must evaluate all hazardous waste streams and determine which should be restricted from land disposal. The Amendments establish deadlines (one-third by 1988, a second-third by 1989 and all by 1990) for such restrictions; if these are missed, automatic prohibition of hazardous wastes in any land disposal facility will result. There is some concern about the timing

of these schedules and the ability of EPA to make timely decisions about specific wastes. Of major concern is not whether alternative technology exists, but whether commercial facilities are available to handle these wastes.

This paper reviews generation and disposal data, identifies and discusses the capacity of available commercial facilities. New technologies are reviewed noting implementation barriers.

Generation and Management Data

In the 1981 survey of hazardous waste generators and waste service facilities prepared for EPA, it is estimated that 265 million metric tons of hazardous waste are generated annually.(9) Although 84 percent of all generators use the commercial waste service industry for treatment and disposal of their wastes, most hazardous wastes (96 percent of the annual volume) are managed at the site of generation or in generator-owned facilities. According to EPA data, the total number of commercial facilities (including treatment, storage incineration and disposal) is 326. EPA defines commercial as those facilities that receive more than 50 percent of the wastes from other firms and are privately owned and operated.

This survey also indicates that most wastes are treated in some manner (66 percent of the total volume). In addition, EPA found that only 20 percent of all hazardous waste is placed in land disposal facilities. EPA defines land disposal very broadly and includes underground injection wells, surface impoundments, land treatment, waste piles, and landfills. Of these types of land disposal, injection wells are most commonly used and surface impoundments second most common. Only 1 percent of the total volume of hazardous waste is placed in the 199 landfills found throughout the United States.

Commercially Available Alternatives

There are five major types of treatment alternatives practiced in the hazardous waste service industry today. These include physical, chemical, biological, thermal and stabilization/solidification treatment processes. The actual application of any one, or any combination of these five, depends on characteristics and properties of the waste (i.e., is it solid, liquid, concentrated or dilutes?).

Physical treatments only separate various phases of the waste (e.g., liquids from solids) and, in general, concentrate hazardous constituents in solid or sludge phases. By concentrating the constituents, further treatment processes or perhaps direct disposal can be done more conveniently. Chemical treatments involve advanced chemical reactions that will either render the waste non-hazardous, e.g., through neutralization, or completely destroy the hazardous compounds, e.g., through hydration. Likewise, biological treatments can destroy or, at a minimum, reduce the hazardous concentrations within the waste. Thermal destructions usually involve combustion of organic material into carbon, oxygen, and water. It must be emphasized that all of these treatment processes generate a residue that may be of lesser, or greater, hazard potential and may be in volumes greater than the original waste. These residues can only be land disposed.

A review conducted by Mackie and Niesen indicates that there is a diverse range of treatment options commercially available.(5) Table 1 illustrates some typical applications. Within the area of physical treatment there are magnetic processes, liquid-solids separation, and membrane separation techniques such as reverse osmosis and electrodialysis.

Chemical treatment alternatives are not new. The technical ability to chemically neutralize or change industrial waste has been available for many years. Innovation focuses primarily on new applications and on the development of more efficient uses of chemical reactions. Commercial applications include oxidation-reduction reactions to degrade trace organics, photolysis to destroy cyanide and dioxin wastes, and precipitation of various metals. Major considerations in the use of these types of treatment processes are

TABLE 1. EXAMPLES OF COMMERCIALY AVAILABLE TREATMENTS

<u>Physical</u>	<u>Typical Applications</u>
Centrifugation	separates liquids and solids
Filter Presses	removes moisture from solids, sludges
Distillation	solvent purification
Carbon Absorption	removes organics
Reverse Osmosis	removes metals and organics
<u>Chemical</u>	
Precipitation	removes metals
Oxidation	destroys organics
Reduction-dechlorination	reduces chlorine content of hydrocarbons
Photolysis	destroys dioxin and cyanide
<u>Biological</u>	
Aerobic/Anaerobic Land Treatment	removes metals and organics degradation of organic sludges
<u>Thermal</u>	
Liquid Injection	destroys organics in liquid wastes
Rotary kiln	destroys organics in sludges and solids
<u>Stabilization/Solidification</u>	
Sorption	uses variety of material to solidify inorganic liquids (e.g., fly ash, lime, clays and carbon)
Pozzolanic Reactions	uses lime-fly ash or portland cement to solidify inorganic wastes.

the potentially low solubility of some metals, impurities in the waste that can inhibit reaction, and potentials for generating equally hazardous by-products.

Biological processes have been used in public wastewater treatment systems for sometime. The limitation of these treatment applications, however, is the presence of biodegradable constituents in a waste stream. Biological reactions are quite sensitive to the presence of toxic elements, either non-biodegradable organic compounds or metals. Land treatment is a form of degradation used commercially for some hazardous waste, primarily refinery sludges. However, using this process, the potential exists for incomplete degradation by natural microorganisms and migration of hazardous constituents from the treatment site to groundwater sources.

Conventional thermal treatment processes (traditional incineration) are useful primarily for organic compounds. These treatment alternatives can be quite efficient, but also very expensive by comparison with physical, chemical or biological processes. There are limitations in the fuel value of a waste and in operational conditions required for maximum destruction efficiency.

Stabilization/solidification processes are alternatives used for wastes containing inorganic elements. In contrast with chemical, biological and thermal treatments, there is no change in the toxic property of the hazardous constituent. However, the potential mobility of these constituents often is reduced dramatically. Although these treatment processes are commercially available, new applications are being

investigated. For example, a joint research effort is underway between Canada and the United States.(6) The purpose is to evaluate the range of stabilization/solidification processes and the integrity of these for a diverse range of wastes.

New Technological Applications

No one questions the technical ability to attain the goal of the 1984 HSWA--to reduce dependence on land disposal. Wastes containing organic compounds will be treated, resulting in near-complete destruction of the hazardous constituents. Inorganic wastes can be solidified to produce environmentally safe treatment residues. Current technical difficulties in applying treatment technologies are most often encountered for those wastes containing mixtures of organics and inorganics.

New technology development is an ongoing process. Some new or innovative applications have arisen in response to needs of the Superfund program, others more directly related to needs of industrial waste management. A recent study by the Congressional Office of Technology Assessment identifies several promising, but not yet commercially available, technologies.(1) A recent review by The Hazardous Waste Consultant identifies several innovative technologies.(3) As illustrated in Table 2, some of these have advanced beyond the laboratory stage and are considered ready for pilot or commercial development.

Barriers to Compliance

A major difficulty in implementing the Congressional mandate to restrict land disposal of wastes is the lack of commercial capacity for

TABLE 2. EXAMPLES OF NEW TECHNOLOGICAL DEVELOPMENTS

Enzyme Destruction	Biological destruction of organics; does not involve living organisms; can be maintained in immobilized systems or applied directly to wastes or contaminated material.
UV Photolysis	Used to detoxify liquids containing dioxin, being developed for application on contaminated solids; dioxin mobilized by surfactants and subjected to UV photolysis; can reduce concentrations by 90 to 99%.
Pyroplasma Processes	Break-down of waste fluids to elemental constituents; being developed as a mobile unit; tested for destruction of chlorinated organics; low power consumption and rapid start-stop mode.
Plasmadust Process	Recovery of metals from iron and steel mill baghouse dust; reduces metal oxide to elemental forms; iron removed with molten slag; zinc and lead removed as gas; tests resulted in yields of 96% for iron, zinc, and lead.
Plasma Arc	Destruction of PCBs and PCB-contaminated equipment; destruction and removal efficiency of 99.9999%; possibility for metal recovery from molten slag
Circulating Bed Incineration	High heat-transfer and turbulence allow operation at temperatures lower than traditional incinerators; accommodates solid and liquid wastes; complete destruction of organics at relatively low temperatures; no need for scrubber system to remove acid gases; particularly cost-efficient for homogeneous wastes from oil and petrochemical processes.
High-temperature Fluid Wall Reactor	Most suitable for contaminated soil; liquid wastes require a carrier; pyrolyze organics to carbon, carbon monoxide and hydrogen; equipment not attacked by inorganic components; mobile units possible; reaches destruction efficiencies of 99.9999%.

Penberthy Pyro-Converter	Glass-melting furnace technology adapted for destruction of organics; suitable for liquids, vapors, solids and sludges; solid residues (inorganics) incorporated into glass matrix; current use for production of HCl and destruction of chlorinated organics, therefore RCRA regulations not applicable.
Pyrolyzing Rotary	Operates in oxygen-free environment and at lower temperatures than conventional kiln; produces gas suitable for energy recovery or further treated to recover condensed hydrocarbons; recovery of metals possible without volatilization; reduced need for air pollution control; need to verify destruction efficiencies of hazardous constituents.
Rollins Rotary Reactor	Suitable for viscous and high-solids content wastes; no need for supplemental fuel; reduced gas scrubbing requirements; high-transfer efficiencies may increase destruction efficiencies at lower temperatures.
Supercritical Water Oxidation	Oxidize organics to carbon dioxide and water; high pressure steam or electricity produced; inorganic salts precipitated; especially efficient with highly concentrated organic wastes; for water containing 10% organics, destruction efficiency greater than 99.99%; suitable for chlorinated solvents and PCBs.
Wet Oxidation	Suitable for dilute aqueous waste that cannot be incinerated or biologically treated; destruction efficiencies expected in range of 99% to 99.99%; oxidizes organics and inorganics; not appropriate for halogenated aromatics.
Vertical-tube Reactor	Adaptation of wet oxidation into 1-mile deep well system; operates at lower pressure than conventional process; currently applied to municipal wastewater.

Source: The Hazardous Waste Consultant, "A Guide to Innovative Hazardous Waste Treatment Processes, "January/February, 1985, pp. 4-1 through 4-32.

TABLE 3. DISTRIBUTION OF COMMERCIAL FACILITIES

<u>STATE</u>	<u>TREATMENT</u>	<u>INCINERATION*</u>
Alabama	1	1
Arkansas	1	1
California	7	1
Connecticut	5	1
Florida	0	1
Georgia	1	0
Illinois	6	2
Idaho	1	0
Indiana	3	0
Iowa	1	0
Kansas	0	1
Kentucky	1	2
Louisiana	4	1
Maryland	1	1
Massachusetts	1	2
Michigan	9	0
New Jersey	6	2
New York	6	3
North Carolina	0	3
Ohio	11	3
Oklahoma	2	0
Oregon	1	0
Pennsylvania	8	0
South Carolina	3	1
Tennessee	2	0
Texas	6	1
Utah	1	0
Virginia	0	2
Washington	3	0

* Many of these facilities have restrictions on concentrations and BTU value; includes cement kilns.

Source: The Hazardous Waste Consultant, "The Outlook for Commercial Hazardous Waste Management Facilities: A Nationwide Perspective," March/April, 1985, pp. 4-1 through 4-49.

treatment and incineration. The EPA 1981 survey emphasized that commercial capacity accounted for only 1 percent of the national total for these alternatives. As illustrated in Table 3, the number of available commercial facilities is limited and not uniformly distributed throughout the country. While total unused commercial capacity was estimated by EPA to be less than 1 percent of the national total, the cumulative capacity utilization of current facilities is estimated to be only 35 percent.

Although it is quite obvious that there is a diverse range of current and new alternatives to land disposal of wastes, several uncertainties inhibit new capacity development: siting problems, market availability, regulatory requirements, expeditious permitting.

Siting

The ability to site a new facility is perhaps the major impediment. The prevalent attitude by potential host communities is that any waste service facility is undesirable. Unfortunately the public has not been willing to acknowledge both the need for alternatives to land disposal and differences in health and environmental risks associated with an incinerator or treatment facility as compared to land disposal facilities. In the last two years, there have been nearly 15 major attempts at new facility development throughout the country.(4) None have been successful.

Market Availability

Future markets obviously impact commercial development. Three factors contribute to uncertainties about potential hazardous waste markets. The first is the continual attempt by states and communities to restrict the

free transport of hazardous waste across state and county borders. In planning a new commercial facility, there must be some certainty about the volume of waste that can be expected at the facility over time. Restrictions on movement of waste across regions, often is accomplished through imposition of high tax rates on out-of-state wastes.

Second, many states further inhibit commercial development by imposing differential tax rates for wastes managed at commercial and generator-owned facilities. Imposition of high taxes only at commercial treatment facilities plus the cost of installing new technologies places these facilities at a competitive disadvantage with land disposal. Also, the greatest potential for "new" technology development on a large-scale rests with the commercial industry. High-capital investment is needed. Generator development may be discouraged because of limited rates of return on such investment. By imposing a high tax on only commercial facilities, a further competitive disadvantage results between commercial and generator-owned facilities thus, impeding future commercial developments.

Finally, the 1984 HSWA mandate minimization of wastes by generators, resulting in some uncertainty as to the size of future markets as well as the composition of these wastes. Although minimization is desirable, it does have a direct impact on commercial development of innovative technologies. Until manufacturing processes have been identified and the volume and the composition of hazardous waste have been estimated, analysis of future market potential will be highly speculative. New investments are not likely until future trends can be identified with some certainty.

Regulatory Impact

Another uncertainty of particular importance to the development of innovative alternatives to land disposal lies with potential regulatory requirements. Currently there are no standards for treatment processes other than incineration. As EPA begins the evaluation for restricting wastes in land disposal, health-based thresholds will be developed. These thresholds will be used as standards by which to judge the effectiveness and efficiency of alternative treatments, those currently available as well as innovative developments.

If new technologies are going to be developed, the capital investment for scale-up and construction will be very high. Thus, uncertainty about the acceptance of such technologies within the regulatory arena can delay necessary commitments to these investments.

Additional uncertainties about potential technical adjustments needed to meet regulatory requirements discourages acceptance of the innovative alternatives. The Agency must begin to evaluate new technologies, indicating criteria for acceptance in the Resource Conservation and Recovery Act (RCRA) and Superfund programs. Executives of treatment companies recently reported to Congress that delays by the Agency in evaluating new technology are major factors in failures to implement them on a commercial scale.(2)

Permitting Process

Finally, a major impediment to development rests with the slow pace and established priorities of the permitting process. Before any treatment facility owner or operator, whether employing traditional or new technology, can engage in hazardous

waste service activities, it is necessary to obtain a permit granted under the RCRA program. The record to-date for permitting is very poor.(8) Of the facilities classified by EPA as storage/treatment facilities, only 353 of an expected 2327 facilities have received permits. The majority of these are for storage of hazardous waste rather than for actual treatment. Only 18 of the 219 potential incineration facilities have received permits; few of these are commercially owned.

Compounding the situation is the permitting schedules mandated by the 1984 Amendments. These schedules require that EPA first give attention to permits for land disposal facilities, next incineration facilities, and finally, to give attention to existing treatment facilities. The new National Permits Strategy attempts to redress this problem by placing higher priorities on commercial treatment and incineration capacity development.(7) EPA has recognized the need to expedite permits for existing commercial incinerators, for expansion of treatment and incineration capacity, as well as for research and demonstration projects. However, the permitting process for the latter will be dependent somewhat on concomitant development of regulatory standards for new technologies.

Conclusion

If the industrial sector of our nation is to implement the congressional mandate for reduced dependence on land disposal, a greater commitment is needed for rapid development of new treatment and incineration facilities. The commercial waste service industry is eager to invest in expansion of

current capacities and development of new innovative technologies. Federal and state officials, the public, and industry must be dedicated to reducing the barriers to commercial development.

Siting problems must be resolved; regulatory standards identified, and permits processed expeditiously. We do not have the luxury of waiting several years to develop appropriate institutional mechanisms to address these problems. If we are to implement treatment alternatives to the fullest extent possible, it is necessary for the government agencies to commit sufficient resources for resolving these implementation barriers.

The country cannot afford to continue the current slow pace in attending to waste management problems. The legislative clock is ticking; like it or not, all wastes may be restricted from land disposal in 5 years. That leaves very little time to expand current commercial capacities and to invest in newer treatment alternatives.

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Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

LABORATORY SCALE TEST SIMULATING CODISPOSAL LANDFILLS

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ABSTRACT

In West-Germany in most cases special facilities are used for the handling of industrial wastes. Because of the extensive measures to avoid environmental pollution, this kind of waste treatment is very costly. Consequently, from the economical point of view, codisposal would be advantageous. Before a certain waste is codisposed, negative effects on the landfill behaviour must be excluded. Because of the complex reactions taking place within sanitary landfills, the prediction in the individual case as to whether or not these conditions can be fulfilled, is very difficult.

For this purpose at the Technical University of Braunschweig, a laboratory scale container test has been developed simulating the conditions within a landfill. With the container test, codisposal of the following industrial wastes has been investigated: electroplating sludge, cyanide wastes, mercury sludge, acid sludge, chlorinated hydrocarbons, plant protective agents.

INTRODUCTION

According to the German law on waste disposal the handling of special wastes requires special measures to avoid environmental pollution. This means that, in present practice these wastes have to be treated in special waste incineration plants or disposed of in special waste landfills. Operating of these facilities is very costly because of the extensive technical installations necessary to prevent environmental hazards. Furthermore, in West-Germany it is very difficult to find new industrial waste landfill sites. Hence prolonging the running time of the

existing plants is an important proposition.

One possibility to achieve this is codisposal. Surely there are a lot of special wastes that may be codisposed. Of particular interest are industrial wastes arising in large amounts but containing only low concentrations of hazardous substances. The main criteria to be fulfilled before codisposal is carried out are:

- To render the long-term integration of the landfill into the biocycle, the biochemical degradation pro-

cesses within the landfill must not be affected.

- Toxic substances not removable during leachate treatment or disturbing the leachate treatment process itself must be prevented from getting into the leachate.
- The buildup of volatile hazardous substances reaching the atmosphere with the landfill gas must be avoided.

If a substance having adverse effects on the landfill is codisposed, the subsequent sanitation will be - if at all possible - very costly. This means, before codisposal is done, an exact prediction of the consequences is recommended. This is very difficult, however, on account of the complex physical, chemical and biochemical processes taking place within a landfill. These uncertainties are the main reason that codisposal in West Germany is quite unusual at present time.

One possible method to predict the behaviour of special wastes after their disposal are leaching tests. With regard to codisposal, there are some serious drawbacks, because neither reciprocations between biological degradation processes and constituents of the special waste nor the adsorption capacity of the municipal solid waste (MSW) are considered. Therefore, one can say that leaching tests in most cases are not sufficient to decide for codisposal.

PURPOSE

At the Technical University of Braunschweig, a research project sponsored by the Federal Ministry of Research and Technology (BMFT) has been performed to develop a test

procedure simulating codisposal landfills. On one hand, this test procedure should be well reproducible and require only little time and money. On the other hand, it should simulate a landfill including movement of water and gas as well as the sorption capacity of the MSW. In particular, within the test, the steps of the decomposition of the refuse including initial aerobic processes, the acidic phase and the methanogenic phase should be run through gradually.

APPROACH

After several preliminary trials, a commercial 120 l polyethylene refuse container was chosen as the base of the test setup. For the test, it is provided with a gas tight PVC cover and installations for gas withdrawal and water exchange. Furthermore, an equipment for leachate recirculation is installed consisting of a leachate collecting tank with a submerged pump and a leachate distributor on top of the test container. Fig. 1 shows the test equipment. It is a closed system providing the possibility to capture all flow of gaseous, liquid and solid matter. One test series usually comprises several containers standing in a room constantly heated to 30°C to get good conditions for the anaerobic processes. To start a test, the containers are filled with a mixture of 2 parts crude MSW and 1 part composted MSW, both shredded to a particle size of less than 5cm and brought to a water content of 65 %. The total weight of the refuse within a container may vary between 60 and 90 kg. One container receives no additional substances serving as a control, while the other ones receive various amounts of the concerned special waste added as a

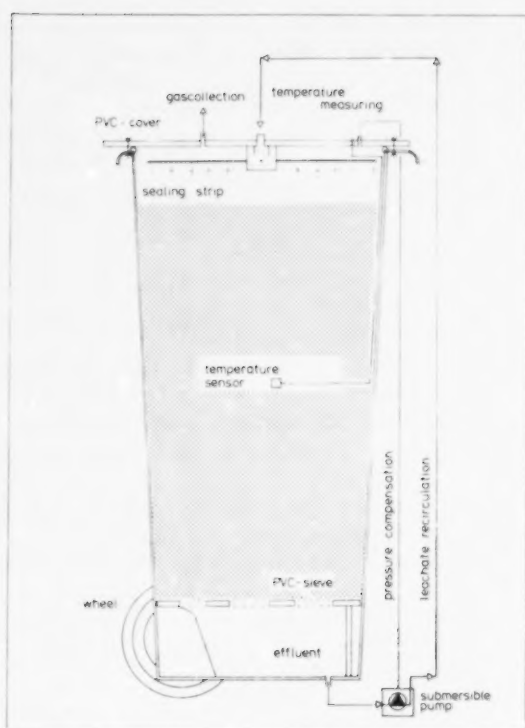


Figure 1. Schematic view of the test container

layer within the upper third of the MSW. After filling, the containers are sealed. During the test period, leachate is pumped back 8 times a day to the top of the container. Once a week, 3.5 l of leachate are withdrawn for analysis and replaced with an equal amount of tap water, simulating precipitation and leachate generation. In addition, once a week a sample of the produced biogas, which is quantitatively collected over the whole test, is taken and analyzed by gas chromatography.

Fig. 2 contains the pattern of some leachate and gas data typically observed during a container test.

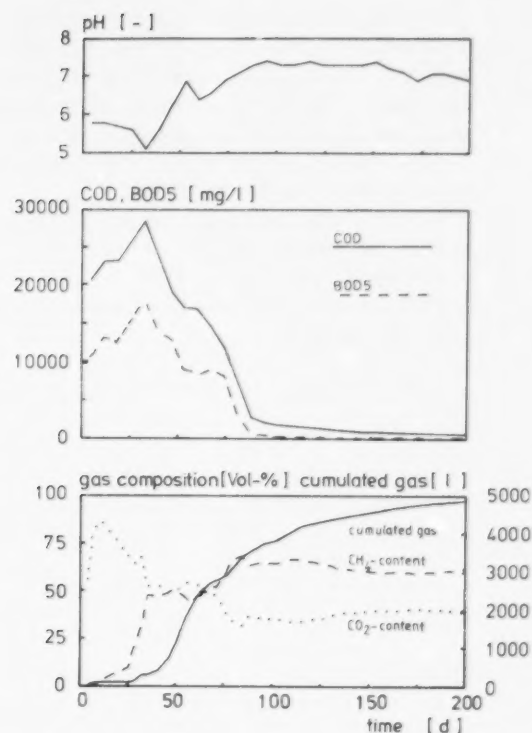


Figure 2. Typical pattern of leachate and gas data during a container test

The acidic phase lasts about 40 days indicated by rising organic pollution (COD, BOD₅) and falling pH of the leachate due to hydrolysis and acidification of organic constituents of the refuse. During this time very little gas is produced. The gradual rising of methane (CH₄) content indicates the beginning of methane buildup from the organic fraction of the leachate. During the period of maximum gas production (i.e. maximum methanogenic activity) gas is characterized by a CH₄ content of about 50 %. The volatile fatty acids (VFA) are converted into CH₄ and CO₂ causing a sharp drop of the organic

pollution and a rising pH of the leachate. After 80-100 days, the end of intensive anaerobic degradation is indicated by diminishing gas production and methane content rising to 60 - 70 % in the produced gas. Note, that at this time leachate concentrations have sunk below 500 mg/l BOD₅ and 3000 mg/l COD. In a landfill, this period might be called "stabilized methanogenic phase".

In general, a test is terminated if:

- the leachate concentrations have reached concentrations below 50 mg/l BOD₅ and 500 mg/l COD,
- the gas production has dropped below 1 - 2 l/day.

This being the case, one may say that anaerobic decomposition of the refuse is nearly completed and a stable state is reached. In general, this takes about 150 - 200 days provided no toxic effects of the added special waste delay the decomposition process.

RESULTS

Test series with electroplating sludge

The first special waste investigated in the container test was an electroplating sludge with considerable amounts of copper, chromium and nickel. Table 1 shows the contents of the various test containers. The MSW was brought to a water content of 65%, as mentioned above. Water content of the electroplating sludge was 23%.

Container No.	MSW	Electroplating sludge	
		kg	% of MSW
1	80	0	0
2	79.2	0.8	1.0
3	76.0	4.0	5.3
4	72.0	8.0	11.1
5	63.8	21.25	33.3

Table 1. Contents of the electroplating sludge test series

The higher the portion of electroplating sludge, the smaller the amount of MSW (i.e. of organic substances) present in a container. Therefore, the initial production of VFA was lower with high portions of the industrial waste. Moreover, the addition of electroplating sludge led to a better buffer capacity of the leachate. These facts had advantageous effects on the anaerobic decomposition processes, as can be seen in Fig. 3.

Compared to the control, the containers with electroplating sludge showed the tendency to produce lower concentrated leachate with a higher pH. As a result, the methane production began first within the containers which had the highest amounts of electroplating sludge. That is, the industrial waste addition had no adverse effects on the anaerobic degradation processes within the refuse. Note, this was the case even at an addition ratio as high as 33%. In practice, the amount applied to container 2 would be more realistic. So one can say, codisposal of this sludge would enhance, but by no means inhibit the anaerobic processes within a landfill.

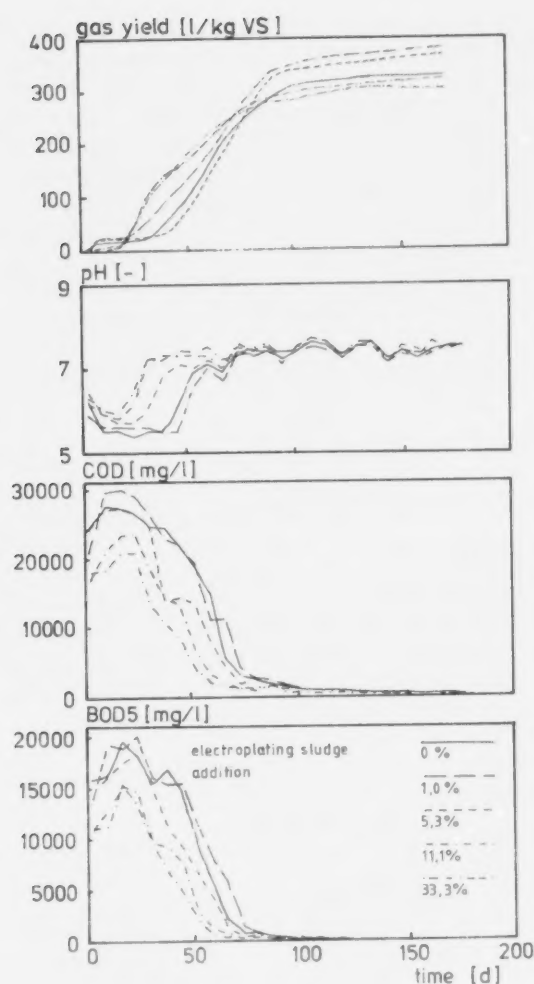


Figure 3. Leachate and gas data of the test series with electroplating sludge

More interesting than this, however, are the effects of codisposal on the leachate quality. In Fig. 4, average metal contents of the leachates produced are presented as a function of the addition of electroplating sludge. There are two curves for each metal, one for the initial acidic phase and another for the methanogenic phase. As can be seen, differences between these two phases are considerable. Nickel

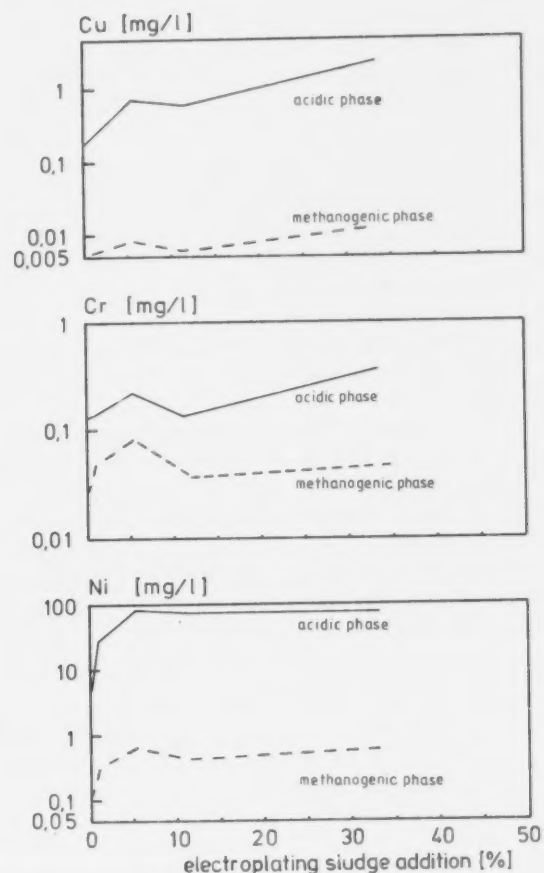


Figure 4. Leachate metal contents vs. ratio of electroplating sludge added

concentrations dropped by 2 orders of magnitude, once a neutral pH-value of the leachate was established. As to the elements Cu and Cr, the influence of rising pH-values at the beginning of the methane production also was observable. As a whole, data presented in Fig. 4 clearly show that in a landfill during the acidic phase, a leachate containing high metal contents will arise, even if codisposal is not carried out. On the other hand, influence of electroplating sludge codisposed is very strong during the

acidic phase. This is true above all for nickel. Therefore, codisposal should not be carried out during the acidic phase.

In addition, Fig. 4 shows the influence of the amount of industrial sludge codisposed. For copper and nickel, this influence was greater during the acidic phase than during the methanogenic phase. However, electroplating sludge addition also affected leachate concentrations in the methanogenic phase. Ni-concentrations rose from 0.1 (control) to 0.3 and 0.7 mg/l at 1% and 5.3% electroplating sludge addition, respectively. At higher ratios, Ni-content remained stable. In opposition to this, Cu- and Cr-concentrations gradually rose over the whole extent of addition ratios. However, leachate loadings didn't rise proportionally with the amount of the industrial sludge.

In general, the load of metals washed out per 1 kg total solids of the electroplating sludge decreased as the addition ratio was raised. Table 2 shows this tendency.

Container No.	Cu	Cr	Ni
2	2.23	0.776	14.5
3	0.805	0.740	6.95
4	0.251	0.081	2.19
5	0.283	0.068	1.25

Table 2: Leachate output of metals related to the amount of electroplating sludge within the containers (mg/kg) during the methanogenic phase

As a result of this series it can be concluded, that the addition of the electroplating sludge causes no toxic effects on the anaerobic

microorganisms present in the refuse. Although an increasing metal loading of the leachate was observed, the MSW was shown to have the capacity to retain a large part of the Ni, Cu and Cr during the methanogenic phase. Therefore, in principle codisposal of this special waste could be a convenient and adequate technique, provided that a proper landfill operation is guaranteed.

Results of tests with additional special wastes

Two additional test series were arranged to investigate the behaviour of various special wastes and some pure substances as codisposed. In this case, it not only was the question of codisposal. We also tried to find out in what way matter getting from non point sources (household, allotments, etc.) into the refuse affects the landfill behaviour.

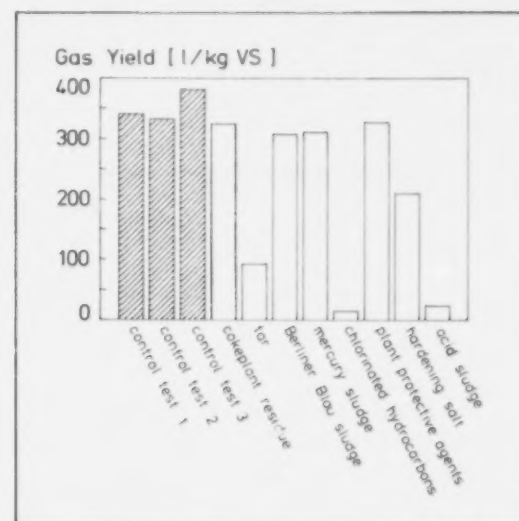


Figure 5. Gas yields of containers with different special wastes

In Fig. 5, gas yields per kg volatile solids (VS) of the MSW within the containers are presented serving as a first indication of the influence on the anaerobic processes within the refuse. Tab. 3 contains data of the special wastes added and the appearance of hazardous substances in the leachates.

The wastes containing hydrocarbons acted quite differently within the refuse. The anaerobic degradation processes were not markedly influenced by the coke plant residue. Gas yield of the tar container however, was very low, although the methane content was as high as 50 %. This indicates

container no. special waste	amount of special w. (%) of MSW	main specific substances	maximum leachate concentration (in parenthesis:control) (mg/l) (mg/l)	
4 coke plant residue	8.2	benzene xylene naphthaline pyridine	3.10 0.539 0.561 2.80	(0.114) (0.580) (0.431) (0.210)
5 tar	8.2	benzene xylene naphthaline pyridine	0.349 0.500 2.20 38.0	(0.114) (0.580) (0.431) (0.210)
6 Berlin blue sludge	8.2	cyanides	9.4	(<0.01)
7 mercury sludge	8.2	mercury	0.78	(0.006)
8 chlorinated hydrocarbons	1.3	dichloromethane trichloroethane trichloroethene tetrachloroethene	329.0 22.0 19.0 6.6	(0.020) (0.012) (0.013) (0.012)
9 plant protective agents	1.1	Atrazine Oxydemeton-methyl Methabenzothiazuron	15.60 4.80 4.24	(<0.01) (<0.01) (<0.01)
10 hardening salt	3.6	barium cyanides	2.8 1130	(1.7) (<0.01)
11 acid sludge	3.6	sulfates sulfites	2150 815	(225) (88)

Table 3. Leachate concentrations of the test series with various special wastes

an inhibition of the anaerobic degradation not in the methanogenic phase, but already occurring during waste acidification. Pyridine is supposed to be the reason for this, because its concentrations were extremely high in the leachate of the tar container (Tab. 3).

Two wastes containing cyanides were investigated:

A sludge arising from the "Berlin-blue" production and a hardening salt. Within the "Berlin-blue" sludge, however, the cyanide content (25 g/kg) was almost completely fixed in complexes. Therefore, addition of this sludge didn't lead to an inhibition of the anaerobic processes within the MSW. This was not the case with the hardening salt, which in addition had a higher CN content (163g/kg). It caused the pH of the leachate to rise up to 10.0 and to remain stable at that level during the first 170 days of the test run. The biochemical degradation didn't start before the CN content of the leachate had dropped below 30 mg/l and a neutral pH value was established.

The high content of mercury (93 g/kg) within the sludge added to container 7 did not lead to any delay of the decomposition processes. This could be explained by the fact that the buffer capacity of the leachate was raised from 660 (controls) to 1070 mg/l as CaCO_3 by the addition of the mercury sludge, which in turn enhanced methane production. The Hg concentration was increased by 2 orders of magnitude. However, the leachate load during the test only represented 0.03 % of the mercury added to the container. That is, MSW can even retain Hg in large amounts. In practice, this sludge with its high Hg content should not be codisposed

On the other hand this test shows, that small amounts of Hg present within a landfill will not lead to any trouble.

Of each volatile chlorinated hydrocarbon (VCH), 125 ml were added to container 8. These amounts led to a total inhibition of the anaerobic processes. Evaluation of that test run is difficult, because VCH proved to migrate through the polyethylene walls of the container in gaseous form. Moreover, leachate concentrations changed by chance over a wide range. As a result, codisposal is surely not a method suited for wastes containing VCH, because they would move uncontrolled in gaseous and liquid form. Furthermore, anaerobic processes would seriously be affected.

The plant protective agents (PPA) didn't affect the degradation processes. In addition, only 0.2 % of the amount of PPA added were found in the leachate. That is, the PPA have been anaerobically degraded to a great deal.

The acid sludge added to container 11 had a low pH and contained large amounts of sulfates and sulfites. All this is suspected to inhibit methane producing bacteria. PH of the leachate remained at about 5 from the beginning and no biological activity could be observed. Even an artificial raising of the pH achieved by lime addition to the refuse surface after 250 and 275 days was not able to encourage methane production. This indicates the high sulfur content present in the container is the main reason for the inhibition of anaerobic degradation processes.

CONCLUSION

Results of the test series show that the container test makes it possible to run through the processes taking place within landfills in a fairly short time. Therefore, the container test is a suitable method to predict the effects of codisposal on landfill behaviour.

The addition of various amounts of an electroplating sludge containing Cu, Ni and Cr caused no adverse effects on the anaerobic processes within the refuse. Metal contents in the leachate were raised, but overall only small portions of the metals present in the containers appeared in the leachate. The results of this test series show that, once a landfill has reached the methane phase, codisposal of the electroplating sludge would cause only slightly increased metal concentrations in the leachate. Hence, codisposal might be applied in this case provided that a tight base liner and a well functioning leachate drainage exist.

In additional test runs, various industrial wastes and hazardous substances proved to act very differently. No effects on gas production were observed after addition of; a mercury sludge, plant protective agents, Berlin Blue sludge containing cyanides or a coke plant residue. Anaerobic activity was markedly impaired both by the addition of the hardening salt and by the tar; almost no gas production could be observed with the

added chlorinated hydrocarbons and the acid sludge. These results give some indications of the problems that might be caused by the tested substances getting into domestic refuse. To obtain more detailed and reliable data, however, at least 3 containers with various amounts of one special waste should be used for the test.

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RAPID APPRAISAL OF RELATIVE RISK BY SOIL APPLIED CHEMICALS FOR GROUNDWATER CONTAMINATION

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ABSTRACT

A simple mathematical screening model is presented that can aid in evaluating the relative risk to groundwater from applying non-polar synthetic organic chemicals to soil. The basic premise is that the magnitude of the quotient of the chemical concentration in the groundwater and the maximum allowable concentration (as established by EPA or Health Departments) represents the health risk of a chemical. The closed form screening model is based on conservative, simplifying assumptions and requires only readily available data such as: basic soil properties (organic matter and saturated hydraulic conductivity), organic chemical properties (octanol-water partition coefficient and degradation rate) and environmental factors (recharge rate and depth to groundwater).

The methodology was applied to assess the relative risk of organic chemicals in municipal sewage sludge and pesticides applied to agricultural land. The results were realistic.

Introduction

Application of organic wastes to land can provide benefits for both the generator and the user, but questions have been raised regarding the potential for pollution of groundwater from constituents of the waste as a consequence of this practice. Synthetic organics are one class of constituents that may be of concern. Municipal sewage sludges, one group of organic wastes applied to land, are known to contain synthetic organics (19). The presence of these chemicals in groundwater represents a health risk to consumers. However, evaluation of that risk has been difficult to assess. This

paper will consider the relative risk to groundwater of synthetic organics from municipal sewage sludge, commonly applied to land.

The fact of groundwater contamination by synthetic organics from municipal and agricultural sources has been well documented (11,13). While a great deal may be learned about the movement of synthetic organics through soil from the detailed study of such examples, researching the movement of each of the millions of synthetic organics in the thousands of soil types would be prohibitively expensive and enormously time consuming. One

approach to the solution of this problem is to develop simple, though fundamental relationships which describe the important soil-synthetic organics interactions as they relate to transport mechanisms. For many of the synthetic organics identified in sludge in important concentrations, data on the necessary chemical properties are available.

Purpose

The purpose of this paper is to describe a model that can aid evaluation of the relative risk of movement of synthetic organics to groundwater. The screening model will be used to identify those chemicals in a particular waste that pose the greatest potential for exceeding maximum tolerable concentrations in groundwater. While identification of the absolute risk of a specific chemical for all soils and environmental conditions will not be attempted in this paper, assessing relative risk of chemicals using a single set of very conservative assumptions for soil and water interactions is straightforward. In addition, such assumptions provide a "worst case" example so that in other settings public health risks from groundwater contamination will likely be much lower.

Modelling in detail the leaching of chemicals applied to soil may be based on a three-step approach. The first step identifies, based on a readily available data, chemicals whose concentrations in groundwater will pose the greatest health risk. The second step models the actual time series of the chemical concentration in water during the year. It requires a more sophisticated

model and also requires more detailed input data. The third step determines the remedial action. For example, (for recycling sludge to the land) the timing and application rate is designed such that the concentration of chemicals of the greatest potential risk remains below the standard.

This paper deals with the methodology for the first step. Models, like Behavior Assessment Model for Trace Organics in Soils (6) or Model for Underground Solute Evaluation (15) may be used for steps 2 and 3.

Modelling Philosophy

A rapid appraisal of potential risk of many chemicals over a broad range of environmental conditions must necessarily be based on readily available data. These data describe basic chemical and physical properties of soil and synthetic organics and are appropriate for rapid screening techniques. The assessment methodology therefore is developed in such a way that only generally available data are required for input. The following simplifying assumptions are made:

- Soil consists of a root zone (with organic matter) and a subsoil. Each layer is homogeneous.
- Steady-state movement has been established as a consequence of regular land applications.
- Chemical has a linear adsorption isotherm and has a first order degradation rate.

In order not to underestimate the hazard, a worst case situation is simulated. Therefore, the following additional conservative

assumptions are made.

- No plant uptake of the chemical occurs.
- No volatilization of low molecular weight chemicals takes place since the chemical is considered to be incorporated.
- No significant adsorption below the root zone occurs because of the lack of organic matter.
- Groundwater directly below the application site is withdrawn for drinking purposes.

Thus, all of the chemical applied to the soil and/or its degradation products are considered to be potentially leachable to groundwater that may be used directly as drinking water.

The Model

The basic premise is that the relative health risk of a chemical that enters the groundwater is represented by the relative magnitude of the ratio of the concentration of the chemical in the groundwater to the allowable concentration of non-carcinogens as established by the U.S. Environmental Protection Agency (EPA) (14,20). For chemicals which are known carcinogens, the most conservative concentration is used which represents an additional cancer risk of 1 in 10,000,000. This risk is approximately equivalent to that of smoking 0.14 cigarettes in a lifetime.

For the development of the model it is important to note, as an example, that the water flowing into a well consists of a composite of the water surrounding the well screen. As these screens are usually several feet in length, the groundwater quality entering

the well through the well screen will not reflect any localized high chemical concentrations occurring during the year. As an example, under dynamic conditions the chemical is assumed to move through the soil as a band of high chemical concentration in the groundwater (Figure 1). As this band of high chemical concentration water moves down past the well screen, water entering the well contains a chemical concentration representative of the average of that for all water entering the well. Under steady-state conditions assumed by this model a uniform chemical concentration would move past the well screen. Therefore it is considered that groundwater chemical concentrations averaged over a year provide an acceptable indication of probable quality in this initial screening model.

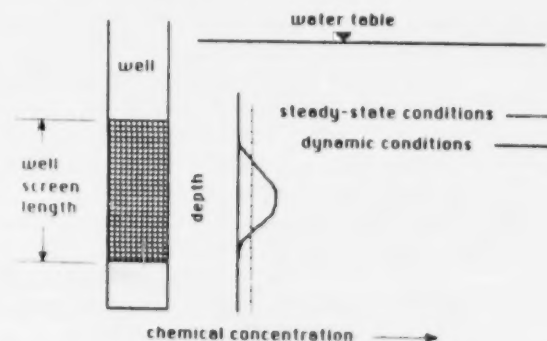


Figure 1. Chemical concentration as a function of depth in groundwater relative to the well screen length.

The concentration of the chemical in the groundwater is a function of the amount of chemical applied, the amount of water in which it is dissolved, the degradation rate, and the time the chemical is in the soil. The time available for degradation is equal to the travel time of the chemical

from the soil surface to the well. For non-polar chemicals which are adsorbed mainly to organic matter, the travel time can be expressed, based on the assumptions made before, as for the zone with organic matter as

$$t_r = \frac{Z (k * \rho + \theta)}{R} \quad (1)$$

for the unsaturated zone below the zone with organic matter as:

$$t_u = \frac{(GWD - Z) \theta}{R} \quad (2)$$

The total travel through the unsaturated zone is obtained by adding both travel times in equations 1 and 2, viz:

$$t = \frac{Z * \rho * k + GWD * \theta}{R} \quad (3)$$

where:

- t is travel time in vadose zone, days
- t_r is travel time in zone with organic matter, days
- t_u is travel time in remaining part of unsaturated zone, days
- Z is depth of zone with organic matter, m
- ρ is density of soil, g/cm³
- k is adsorption partition coefficient, cm³/g
- GWD is depth to groundwater, m
- θ is average moisture content in subsoil above water table, cm³/cm³
- R is average rate of recharge, m/day

Three variables in equation 3 are not directly measurable. These are the moisture content in the unsaturated zone, the adsorp-

tion partition coefficient and the amount of recharge. Each will be discussed.

The moisture content in the unsaturated zone is a function of the yearly amount of recharge and the hydraulic conductivity (15) and may be expressed as

$$\theta = \theta_s \left[\frac{1}{13} \ln \left(\frac{R}{K_s} \right) + 1 \right] \quad (4)$$

where:

K_s is the saturated hydraulic conductivity in m/day.

The advantage of using the saturated hydraulic conductivity (K_s) rather than the moisture content is that K_s is a function of the soil properties. Average saturated conductivities are known for a wide range of soils.

The adsorption partition coefficient may be found from the octanol/water partition coefficient and the amount of organic matter in the soil as follows (2):

$$k = OM * 10^{(0.52 \log_{10} K_{ow} + 0.62)} \quad (5)$$

where:

K_{ow} is the octanol water partition coefficient, cm³/g
OM is the organic matter content in the root zone, g/g

The octanol-water partition coefficient is known or may be calculated (7) for most chemicals.

Recharge is the amount of water that annually reaches the groundwater. The most accurate value for the recharge may be

obtained from long-term field measurements. For Long Island a value of 60 cm per year was found (16) and for the midwest 3 to 10 cm per year is generally assumed (12). However, the measurements are generally scarce. There also are various ways to estimate this parameter such as the Thornthwaite Mather procedure (17). Also models such as MOUSE (15) may be used to estimate this parameter.

The average concentration of the chemical in the groundwater may be estimated from equation 3 using a first order degradation rate in the unsaturated zone and neglecting the degradation of the chemical in the groundwater.

$$C_w = 0.1 \frac{M}{R} * \exp \left[- \frac{0.69}{R t_{1/2}} \right] * (Z * \rho * k + GWD * \theta) \quad (6)$$

where:

- C_w is the concentration of the chemical in the groundwater, mg/l
- M is the amount of chemical applied to the soil per year, expressed in kg/day
- $t_{1/2}$ is the half-life of the chemical in the soil, days

Equations 3 and 6 give a surprising insight in the concentration of the chemical that might be expected in the groundwater under steady state conditions where the chemical is applied regularly. For example, for non-degradable chemicals that have variable strengths of adsorption to the soil, the ultimate concentration in the groundwater will be the same irrespective of the adsorption partition coefficient. The

only difference will be the time of arrival such that the most strongly adsorbed chemical will arrive much later than the more weakly adsorbed chemical.

For chemicals with the same half-life, and different adsorption partition coefficients, the chemical with the higher adsorption coefficient will have a lower concentration in the groundwater because its travel time to the well is longer.

Thus, the general assumption that the more strongly adsorbed chemicals do not cause groundwater problems must now be reconsidered. As an example, in Minnesota arsenates used to control a grasshopper outbreak in the 1930's were first discovered 38 years later (5).

Finally, a ranking of the hazard of the chemical may be obtained by dividing the concentration of chemical in the well water by the health criteria standard (14,20).

$$h = \frac{C_w}{H}$$

where:

- h is the health risk index
- H is the health criteria, mg/l

For a specific material containing synthetic organics applied to soil, the chemical with the highest risk index is of the greatest potential concern. However, the chemicals with a risk index less than 1 are not likely to leach to groundwater in concentrations in excess of the health standard and will not likely pose

a potential health risk. Further analysis (step 2 and 3) would be required to quantify the risk of those chemicals having a risk index greater than 1.

Input Data

The input data for the model are listed in Table 1. Soil and hydrologic input parameters are site specific such as the depth of the layer with organic matter, the organic matter content, the depth to groundwater and the saturated conductivity of the unsaturated zone. The amount of water recharged depends on the cover crop and the amount of precipitation received by the area.

Chemical input data are dependent on the specific chemical and its source. The amount of chemical applied is a function of the use of the chemical (e.g., a pesticide) or its source (e.g., sewage sludge applied to land). Pesticide applications are commonly 0.5 to 3 kg/ha annually (1). Naylor and Loehr (8,9) have estimated amounts of synthetic organic chemicals potentially applied to land through recycling sludge to soil. The octanol-water partition coefficient, the half-life, and the health standard are specific to the chemical.

Results

To test the model for its usefulness and its realism, several chemicals known to be present in sludge, as well as pesticides, some of which are known to leach to groundwater, were screened for Long Island (New York) and the midwest environmental conditions. Long Island was selected because it is representa-

tive of many soil and precipitation conditions along the Atlantic Coast and because of our previous extensive research with soil and water interactions in that area (15). Midwest conditions were studied because of large scale agricultural production.

The specific conditions assumed for Long Island were: 1) sandy soil with a hydraulic conductivity of 10 m/day; 2) low organic matter content (0.5%) to a depth of 0.3 m; 3) a depth to groundwater of two meters; and 4) an annual recharge of 0.60 m/year. A second set of conditions were assumed for a midwest loamy soil (Table 1).

Table 2 lists a number of the organic chemicals found commonly in municipal sewage sludge in important concentrations for which the risk was calculated. The application rate of the organic chemical presented in Table 2 was projected from the concentration of the chemical in combined sewage sludges considered to be applied to soil at rates to provide 100 kg/ha of available nitrogen. The application rate shown is the median value of the 13 sludges evaluated (8,9).

To provide a perspective, several pesticides known to leach to groundwater in Long Island soils were also evaluated (Table 3).

The results of the screening model are shown in Table 4. Chemicals found commonly in sludge having a risk index greater than 1 when applied to a sandy soil are the small halogenated short chain hydrocarbons: chloroform, dichloromethane, trichloroethane and

TABLE 1. SPECIFIC DATA FOR INPUT IN THE PROGRAM.

		Input values	
		Sandy soil ^a	Loamy soil ^b
amount of chemical applied per year			
per unit area	(kg/ha/yr)		
half-life of chemical	(day)	Table 2	
depth to groundwater	(m)	2	3
depth of zone with organic matter . .	(m)	0.3	0.6
yearly average recharge	(m/yr)	0.6	0.2
saturated hydraulic conductivity	(m/day)	10	3
K octanol-water	(cm ³ /g)	Table 2	
organic matter content of root zone .	(g/g)	0.005	0.05
health criterion by EPA	(mg/l)	Table 2	

^aLong Island. ^bMidwest.

TABLE 2. EXAMPLE CHEMICALS PRESENT IN SLUDGE.

Chemical	(kg/ha) Application Rate ^a	(day) Half-life of Chemical ^b	(cm ³ /g) Log ₁₀ K _{OW} ^b	(mg/l) Health Standard ^c	(mg/l) Carcinogen risk ^{c,d}
dichloromethane	0.022	110	1.25	---	1.9x10 ⁻⁵
polynuclear					
hydrocarbon ^e	0.39	44	5.52	---	2.8x10 ⁻⁷
1,4-dichloro-					
benzene	0.016	3.0	3.39	0.40	----
chloroform	0.0008	93	1.97	---	1.9x10 ⁻⁵
ethylbenzene	0.062	0.62	3.15	1.4	----
benzene	0.0038	2.1	2.04	---	6.6x10 ⁻⁵
phenol	0.026	4	1.46	3.5	----
di-n-					
butylphtalate	0.046	5	5.2	34	----
toluene	0.15	-0.62	2.69	14.3	----
bis-2-ethyl-					
hexylphtalate	1.2	30	5.3	15	----
1,1,2-trichloro-					
ethane	0.034	1000	2.17	---	6x10 ⁻⁵
trichloroethylene	0.0125	4 & 321	2.29	---	2.7x10 ⁻⁴

^aRef. 8, 9. ^bRef. 3, 18. ^cRef. 14, 20. ^dProtection of human health from potential carcinogenic effects through ingestion of contaminated (surface) water and contaminated aquatic organisms, with an increased cancer risk of 1 in 10,000,000. ^eTotal polynuclear aromatic hydrocarbon includes phenanthrene, anthracene, dibenzo (a, h) anthracene, naphthalene, pyrene, chrysene, and fluoranthene.

TABLE 3. EXAMPLE PESTICIDES USED COMMONLY IN AGRICULTURE.

Chemical	(kg/ha) Application Rate ^a	(day) Half-life of Chemical ^b	Log_{10} k_{ow} ^b	(mg/l) Health Standard ^c
Aldicarb	3	21, 100	1.15	0.007
Carbaryl (Sevin)	2	23	2.35	0.57
2,4-D	0.5	15	1.3	0.10
Atrazine	2	71	2.2	0.15

^aRef. 1.^bRef. 6, 18.^cRef. 14.

TABLE 4. HEALTH RISK INDEX OF SOME SYNTHETIC ORGANICS AND PESTICIDES APPLIED TO LAND.

		Groundwater Health Risk Index	
Chemical		Sandy Soil ^a	Loamy Soil ^b
trichloroethylene	$t_{1/2} = 4$ (oxidation)	=0	=0
	$t_{1/2} = 321$ (hydrolysis)	4.2	0.0002
dichloromethane		47.6	0.0004
polynuclear hydrocarbon		=0	=0
1,1,2-trichloroethane		78.5	9.1
1,4-dichlorobenzene		=0	=0
chloroform		1.1	=0
ethylbenzene		=0	=0
benzene		=0	=0
phenol		=0	=0
di-n-butylphthalate		=0	=0
toluene		=0	=0
bis-2-ethylhexylphthalate		=0	=0
aldicarb	$t_{1/2} = 21$ days	0.05	=0
	$t_{1/2} = 100$ days	15.6	0.0001
carbaryl		=0	=0
atrazine		0.16	=0
2,4-D		=0	=0

^aLong Island. ^bMidwest.

trichloroethylene. These chemicals have a relatively long half-life coupled with a low adsorption coefficient. While the presence of these chemicals is well documented (11), they tend to volatilize and are unlikely to leach into groundwater where sludge is not immediately incorporated into the soil (10). In an extensive study of groundwater quality beneath a Michigan sandy soil sludge application site, none of the synthetic organic chemicals were present at detectable concentrations (4). Thus, results of the model indicate that monitoring efforts should focus on the short chain halogenated compounds. The larger, bulky molecules such as phthalates and other ring compounds appear to present little risk to groundwater contamination from surface application.

Of the pesticides reviewed, only aldicarb was found to have a health risk index greater than 1, and then only for sandy soil with little organic matter. Aldicarb contamination of groundwater has been reported under such treated soils in New York, Wisconsin, and Florida. For the other pesticides tested in the model, there appears little risk to groundwater contamination where the pesticides are used at recommended rates.

Conclusions

The mathematical model developed in this paper appears useful for the rapid appraisal of relative health risks of synthetic organic chemicals applied to soil. The model was based on fundamental relationships of soil-water interactions with synthetic organic chemicals.

Assumptions incorporated into the model were very conservative so that potential hazards are greatly overestimated. Thus, risks should be viewed only as an index of potential groundwater contamination.

The model has been demonstrated to be useful to rapidly assess which synthetic organic chemicals pose the greatest risk to groundwater. Using the risk index as a guide, management practices or monitoring programs can be designed to minimize such risks or provide a special emphasis on those chemicals having the greatest risk.

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PHYSICAL AND CHEMICAL ATTENUATION PROPERTIES OF TIDAL MARSH SOILS AT THREE MUNICIPAL LANDFILL SITES

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ABSTRACT

The hydraulic conductivity, (K), cation exchange capacity, (CEC), and total organic carbon, (TOC), of soils composed of clays and silts are thought to make them effective barriers to contaminants in groundwater, and media capable of sorbing heavy metals and organic compounds. Tidal marsh deposits consisting of silts and clays and underlying sands at three municipal landfills were tested for pH, CEC, TOC and K. Results were compared with heavy metal and organic compound concentrations measured in groundwater samples above and below the tidal marsh deposits. Evaluation indicated that the tidal marsh desposits were less effective in removing heavy metals than expected, but were effective in preventing migration of organic compounds into underlying sand deposits. Total volatile organics, (TVO), and total halogenated volatile organics, (TVHO), were reduced from 72,440 ug/l to 27 ug/l, and 867 ug/l to <10 ug/l in some cases. Organic carbon content in the tidal marsh deposits averaged 2.2%. Decomposition of the organic fraction yielded acids which reduced pH to as low as 3.3. Consequently, the tidal marsh deposits were ineffective in removing heavy metals, but remained effective as an hydraulic barrier. Our studies showed that the soils effectiveness to mitigate groundwater degradation from heavy metals and organics can be gauged by evaluating the soil's chemical and physical properties.

INTRODUCTION AND PURPOSE

Tidal marsh deposits consisting of organic silt and clay are generally considered effective hydraulic barriers to ground water flow and having the adsorptive capacity to retain dissolved heavy metals and organics. However, natural factors may alter, negate or reduce these properties.

Such factors include:

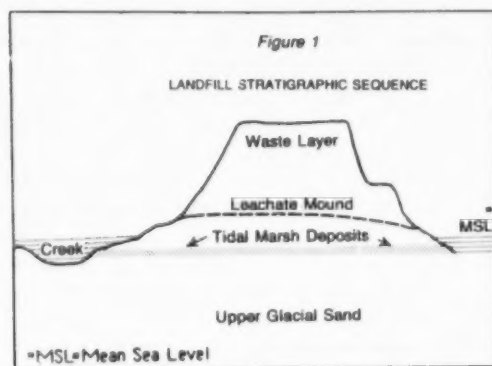
- Soil pH, cation exchange capacity, and total organic carbon
- Inclusions in the deposits (pockets of sand and/or shell fragments)
- Discontinuities within the silt and clay deposit

- Hydraulic conductivity of deposits

This paper addresses our findings on soil pH, CEC, and TOC and their effects on the adsorptive capacity of tidal marsh deposits.

Gibbs & Hill completed a hydrogeologic study at three municipal landfills located in the New York Metropolitan area. The investigation aimed at assessing the impacts of landfill-generated leachate on local aquifers and bay waters.

At each landfill, the stratigraphic sequence consisted of the following (see Figure 1):



- Municipal waste: 30' to 120'
- Tidal marsh deposits: 5'-12'
- Hydraulic fill: 5'
- Wisconsin-Age glacial outwash sediments (Upper Glacial sand aquifer) to 150'
- Other Pleistocene and Cretaceous Sediments
- Pre-Cambrian crystalline bedrock

The aquifers underlying each site are:

- Water Table Aquifer: (Leachate Mound)
- Confined Aquifers: Upper Glacial, Jameco, Magothy, and Lloyd (top to bottom)

Of these aquifers, the study focused on the Upper Glacial.

Ground water level measurements within the aquifers varied as follows:

- Leachate mound: 8' to 11' MSL (Mean Sea Level)
- Upper Glacial Aquifer: -2 to -6' MSL

The difference between piezometric heads caused a downward driving force, which resulted in leakage of ground water and landfill leachate from the leachate mound into the Upper Glacial Aquifer, through the tidal marsh deposit.

Chemical soil testing was performed on samples from the tidal marsh deposits and the Upper Glacial sands. The tidal marsh deposits consisted primarily of silt and clay with occasional lenses of fine sand and shells. Organic content included humic materials and layers of peat. The Upper Glacial sands were composed mainly of sand and gravel.

Municipal refuse makes up the bulk of the material disposed at the landfills. Daily disposal rates run as high as 9,500 tons at the largest landfill, 297 acres. Waste oil was applied to landfill roads in earlier years to control road dust. Illegal dumping of hazardous wastes occurred at all three sites; and 5,000 fifty-five gallon drums containing wastes of paint pigments and solvents, were recently unearthed at one location and

waste oil laced with PCB's at another.

APPROACH

Fifteen soil samples were obtained during the installation of ground water monitoring wells. Samples were collected using a steel split-spoon sampler and undisturbed samples were retrieved using a brass thin wall "shelby" tube.

Samples were sent to the lab and analyzed for:

- pH
- Cation Exchange Capacity (CEC)
- Total Organic Carbon (TOC)
- Hydraulic conductivity (K)
- Grain size distribution and identification.

Well water samples from above (U wells), and below (S wells), the tidal marsh deposits were compared for heavy metals and organics. The results were then examined against soil sample test results, and the physical character of the tidal marsh deposits. We gauged the effectiveness of the tidal marsh deposits to filter heavy metals and organics based on these comparisons.

A total of 65 wells were used in this study. Wells above the tidal marsh deposits numbered 32 and were located between +1.0 and -7.0 mean sea level - just above the deposits. The 23 S wells were placed between -30 and -40 feet below mean sea level in the Upper Glacial Aquifer. The remaining 10 wells were placed in the Upper Glacial

Aquifer between -110 and -140 feet below mean sea level.

EVALUATION FACTORS/PROBLEMS

A number of factors are extremely important to consider when assessing the potential of the deposits to mitigate wastes. First, the information obtained may be used to obtain a relative measure of effectiveness against chemical migration. Second, in order to properly evaluate the soil chemical data, it is essential to get an accurate picture of the deposits.

Large voids, windows or significant layers of coarse materials allow ready movement of leachate from one layer to another. If these are not recognized and their dimensions and character known, even favorable CEC, pH and TOC data may yield erroneous interpretations. In addition, undisturbed samples should be examined to see what portions are the most frequently occurring, and which portions show the outside range of variability in the samples. Third, it is important to test CEC at ambient pH in addition to pH 7. This is important because the soils should be evaluated under in-situ conditions, conditions unlikely to change in the near future.

One problem we had was the lack of leachate extraction analyses on the soil samples. This information would have given a better account of where the metals and organics were moving and how much was being sorbed.

RESULTS

Cation Exchange Capacity

The tidal marsh deposits samples had CEC values of 7.0 to 237 milliequivalents (me)/100g soil, with most values falling

between 39 and 184 me/100g. These values are relatively high and were attributed to humus content of the soil.

CEC values in the Upper Glacial sand ranged from 0.6 to 59 me/100g, with an average CEC of 22 me/100g.

Overall, CEC values in the tidal marsh deposits were one order of magnitude greater than in the Upper Glacial sands (See Table 1).

TABLE 1A
TIDAL MARSH DEPOSITS
SOILS CHEMISTRY: pH, TOC, CEC

Sample Data	Landfill 1			Landfill 2			Landfill 3
Well No.	HF102D	HF111	HF201	HF203U	HE202S	HE203S	HE203S
pH	3.6	3.8	3.5	5.5	3.5	4.8	3.3
TOC, ug/g	27,100	14,900	1,600	20,800	7,580	1,010	25,500
CEC, meq/100g @ pH 7	184	237	24	175	39	7	180
Material Type	ML-1	ML-2	SM-SG	ML-CL	CL	ML-3	ML-4

Material Type:

- ML-1: Soft grey silt, some clay, trace shell fragments.
- ML-2: Soft grey silt, little clay, trace peat
- SM-SG: Olive brown medium sand, some silt grading to well graded sand with trace silt, clay and gravel
- ML-CL: Silt and Clay with an eight inch layer of shell fragments.
- CL: Clay with some silt, trace fine sand, grading to fine sand and little silt.
- ML-3: Silt with little clay and shell fragments, trace very fine sand.
- ML-4: Silt and clay.

TABLE 1B
UPPER GLACIAL SANDS AQUIFER
SOILS CHEMISTRY: pH, TOC, CEC

Sample Data	Landfill 1			Landfill 2			Landfill 3
Well No.	HF102D*	HF115	HF201S	HP201	HP203	HP204	HE202S
pH	3.5	6.6	6.0	5.9	6.1	6.5	3.0
TOC, ug/g	550	410	750	600	420	960	320
CEC, meq/100g @ pH 7	20	59	152**	0.6	8	13	47
Material Type	SM-1	SM-2	SP-SW	SM-SF	SW	SM-3	SM-4

* Above Tidal Marsh Deposits - Not part of Upper Glacial Sands Aquifer

** Possible sample contamination

Material Type:

- SM-1: Brown fine to medium sand, dense, little silt.
- SM-2: Brown medium to coarse sand, moderately dense, little silt
- SP-SW: Grey medium to coarse sand, slightly dense with trace silt and some gravel.
- SM-SF: Grey medium to coarse sand, slightly dense, trace silt and fine gravel.
- SW: Fine to coarse sand with trace silt and fine gravel.
- SM-3: Olive brown medium to coarse sand, loose, with trace silt and brick fragments.
- SM-4: Fine to medium sand with some silt.
- SM-SW: Fine to coarse sand with trace silt.

Soil pH

Low values for soil pH (acid conditions) indicated increased potential for mobility of metallic ions.

Tidal marsh deposits samples exhibited soil pH values of 3.3 to 5.5, with most of the samples being extremely acid (pH <4.5) (USDA, 1951). pH in the Upper Glacial sands ranged from extremely acid to moderately alkaline (pH 3.0-8.3), but most samples were in the medium to slightly acid range (pH 5.6 to 6.6).

Lower pH values in the tidal marsh deposits were attributed to acids produced from decomposing organic matter.

The pH in groundwater samples above the tidal marsh deposits ranged between 6.3 and 7.8. Below these deposits they ranged between 6.2 and 7.4.

Soil Organic Carbon

The organic carbon content affects a soil's potential to remove contaminants by providing sites for ion exchange and adsorption, as well as enhancing its capacity to filter out suspended particles, such as PCB's (Weber et al, 1983).

TOC content of the tidal marsh deposits ranged between 0.10 to 2.7%, with a average of approximately 2.2%.

The TOC of the Upper Glacial sands was much lower, ranging between 0.03 and 0.16%, with an average of 0.07%.

Relationship between pH, TOC and CEC

A balance exists in the soil between the pH, CEC and organic matter content. The two components of CEC are:

- pH-independent CEC:

This component is determined by the cations which are fixed in the soil mineral during formation.

- pH-dependent CEC:

This component is related primarily to the organic fraction of the soil, particularly organic functional groups associated with the humus. As the pH increases above 5, these groups increase their ability to adsorb metallic ions.

The tidal marsh deposits in our study included both CEC components. Four samples with TOC content greater than 1% had high CEC values of 175 to 237 me/100g. Three samples with less than 1% TOC content had CEC's of 7.0 to 39 me/100g.

The Upper Glacial sands had little or no organic matter content, and low CEC values. TOC ranged from 0.03 to 0.1% and CEC values ranged from 0.6 to 59 me/100g. Consequently, CEC values in the Upper Glacial sand layers were mostly pH-independent.

Soil Attenuation Potential

Soil attenuation potential results from a combination of chemical and physical factors. Due to the large differences in pH, CEC, TOC and physical characteristics, attenuation in the tidal marsh deposits and Upper Glacial sands in our study differed as discussed below.

Tidal Marsh Deposits

Attenuation potential

appeared to be limited. Despite thickness (5' to 12') and relatively high TOC (>1%), the water quality data did not show any consistent reduction of heavy metals attributable to this layer, as evidenced by a comparison of heavy metal concentrations between water samples from above and below the tidal marsh deposits.

At landfill 1, Ni concentrations at 102U were 50 ug/l and 276 ug/l at 102S. In well 104U, Cr concentration was 38 ug/l, while at 104S it was 32 ug/l. At landfill 2, Sb concentrations in 101U were 540 ug/l and 500 ug/l at 101S. At 103U Cd was 28 ug/l and 38 ug/l at 103S (See Table 2).

Heavy metal concentrations in groundwater samples were generally one order of magnitude greater than background bay water samples taken near the bay center and inlet. Background bay water samples taken near the landfill were generally close in heavy metal content to the groundwater samples. Tidal fluctuations, which bring bay water through the Upper Glacial sands toward the landfills, may explain why some wells show concentrations of heavy metals which are greater below the tidal marsh deposits than above. It is also possible that very low pH levels are causing a release of metals at some locations.

Measurements taken at monitoring wells above the tidal marsh deposits showed the effect of tidal fluctuations on the leachate mound to be negligible. Below the tidal marsh deposits groundwater levels ranged between 0.95 and 2.57 feet.

TABLE 2
1984 GROUNDWATER QUALITY, (ug/l and pH in units)

LANDFILL 1													
Well, HF:	Sb (100)	As (2)	Se (10)	Cd (4)	Cr (20)	Cu (20)	Pb (40)	Hg (0.2)	Ni (40)	Se (2)	Ag (40)	Th (100)	Zn (100)
101 U	L	L	L	8	L	L	80	L	94	L	L	L	84 7.8
101 S	100	L	L	10	L	L	L	L	92	L	L	L	48 6.6
102 U	L	L	L	L	L	L	L	L	50	L	L	L	30 6.8
102 S	460	L	L	40	32	L	240	L	276	L	L	L	52 6.7
103 U	L	6	L	6	L	54	L	L	L	L	L	L	68 6.9
103 S	240	L	L	26	26	76	140	L	210	L	L	220	58 6.8
104 U	L	L	L	20	38	74	80	L	160	L	L	120	358 7.5
104 S	220	L	L	36	32	70	200	L	274	L	L	340	52 7.0
201 U	L	6	L	6	46	50	60	L	198	L	L	L	78 7.7
201 S	220	L	L	21	28	57	170	L	198	L	L	240	93 6.6

LANDFILL 2													
Well, HF:	Sb (100)	As (2)	Se (10)	Cd (4)	Cr (20)	Cu (20)	Pb (40)	Hg (0.2)	Ni (40)	Se (2)	Ag (40)	Th (100)	Zn (100)
101 U	540	L	L	40	62	50	140	2	112	L	L	L	72 6.7
101 S	500	L	L	18	48	L	40	L	94	L	L	L	46 7.2
102 U	200	6	L	26	38	L	120	L	48	L	L	L	28 7.2
102 S	L	L	L	L	L	L	L	L	L	L	L	L	6.5
103 U	L	L	L	28	26	L	100	L	56	L	L	L	62 7.0
103 S	400	L	L	38	52	L	220	L	110	L	L	L	66 6.7
201 U	L	L	L	6	22	L	60	L	224	L	L	140	104 7.4
201 S	180	L	L	14	20	L	120	L	188	L	L	L	56 6.2
203 U	L	L	L	26	28	L	120	L	60	L	L	L	96 7.0
203 S	380	L	L	36	46	L	180	4	90	L	L	L	56 7.0

LANDFILL 3													
Well, HF:	Sb (100)	As (2)	Se (10)	Cd (4)	Cr (20)	Cu (20)	Pb (40)	Hg (0.2)	Ni (40)	Se (2)	Ag (40)	Th (100)	Zn (100)
3N(s)	-	-	-	20	-	-	100	L	-	-	-	-	66 7.5
3S(u)	-	-	-	6	-	-	L	L	-	-	-	-	54 5.7
101 U	L	L	L	L	L	L	80	L	L	L	L	L	70 6.3
101 S	140	L	L	18	24	L	L	0.48	L	L	L	L	96 6.7
102 U	320	L	L	L	22	L	80	L	L	L	L	L	82 7.0
102 S	760	L	L	10	24	L	80	L	52	L	L	L	72 7.1
103 U	120	L	L	L	24	L	60	L	50	L	L	L	140 6.9
103 S	1,560	L	L	46	58	L	260	L	240	L	L	340	114 7.3
202 U	220	L	L	L	L	L	L	L	L	L	L	L	132 6.7
202 S	L	L	L	L	L	L	L	L	L	L	L	L	54 7.0
203 U	-	L	L	30	-	L	100	L	-	-	-	-	10 7.2
203 S	-	-	-	30	-	-	L	L	-	-	-	-	304 7.4

L = Less than detection limit
() = Detection limit

The lack of contaminant removal by the tidal marsh deposits is believed to be due to:

- High acidity in the tidal marsh deposits which lowers the effective CEC.
- High concentrations of Na, Al and Mn present in the bay water, and released from soil at low pH, compete for adsorption sites.

- Reduction and subsequent increased mobility of cations caused by saturated (anerobic) conditions.

- Physical gaps and inclusions of more permeable sediments in the tidal marsh deposits allow leachate to percolate directly into the Upper Glacial sands.

Large differences in concentrations of total volatile organics were found in water above and below tidal marsh deposits. It appeared that the relatively high TOC content of the tidal marsh deposits caused this reduction; a result of the affinity of organic material in the deposits for hydrophobic compounds contained in leachate (See Table 3).

TABLE 3

TOTAL VOLATILE ORGANICS (TVO)
TOTAL VOLATILE HALOGENATED ORGANICS (TVHO)

Land- fill	Well	TVO (10)	TVHO (10)
3	3 N S	246	L
3	3 N U	L	L
3	101 U	49,083	31,775
3	101 S	3,390	2,549
3	103 U	L	L
3	103 S	181	L
2	102 U	1,540	82
2	102 S	L	L
2	201 U	72,440	867
2	201 S	27	L

L = Less than Detection Limit
() = Detection Limit
U = Well in Leachate Mound
S = Well in Upper Glacial Sand
Values in ug/l

Upper Glacial Sand

The Upper Glacial sand layer has a very low potential for attenuating the passage of contaminants because of:

- Large particles size (low clay content) and low CEC
- Low organic matter content

These factors result in a medium which has little or no capacity to attenuate wastes.

SUMMARY

Overall attenuation potential in the tidal marsh deposits was low. Unfavorable pH, high concentrations of competing ions, and anerobic conditions resulted in deposits which have a low capacity to attenuate heavy metals in leachate. The tidal marsh deposits apparently accomplished some removal of dissolved organic compounds, but the most significant effect was the physical restriction of the vertical flow of leachate from the landfill to Upper Glacial sand.

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LAND DISPOSAL OF WASTES CONTAINING POLYNUCLEAR AROMATIC COMPOUNDS

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ABSTRACT

This research project investigated the treatment potential of soil systems for polynuclear aromatic compounds (PAHs) identified in wastes from industrial and municipal sources. A protocol for obtaining the soil assimilative capacities of PAH compounds, including transformation of mutagenic characteristics was developed. The protocol included: (1) incubation, (2) characterization/identification, and (3) determination of mutagenic potential. The protocol involved interfacing high performance liquid chromatography (HPLC) for compound and metabolite characterization with the Ames *Salmonella typhimurium* mammalian microsome mutagenicity assay for determination of genotoxic potential of PNA compounds and transformation products in single constituent systems and in complex waste:soil mixtures.

Kinetics of transformation were related to PAH structure. The range of half-lives was similar for low and high soil loadings (19-190 days) while the initial soil concentration varied over a range of 0.07 to 147 ppm. The initial rate of degradation varied by a factor of 2000. Results of engineering management options suggest that it may be possible to influence the degradation rates of PAH constituents with pH amendment, analog enrichment, complex substrate amendment, and moisture control. Results for mutagenicity testing indicate that the polar class fraction of PAH metabolites may be mutagenic, and may leach through soil under saturated conditions, but proceeds through a pathway of detoxification and degradation which can be controlled and managed. Results of studies obtained thus far indicate that, with a better understanding of soil:waste processes, it will be possible to accomplish safe ultimate disposal and ensure the protection of public health at reasonable cost to society.

INTRODUCTION

Land disposal was defined and approached in this study under the

concept of land treatment. Hazardous waste land treatment (HWLT) can be considered as the intimate mixing or dispersion of wastes into the upper

zone of the soil-plant system with the objective of microbial stabilization, detoxication, immobilization, or plant treatment. HWLT, with proper design and management, must lead to an environmentally acceptable assimilation of the waste which ensures protection of the public health.

Polynuclear aromatic hydrocarbons (PAH) include a group of organic priority pollutants of critical environmental and health concern due to the following characteristics: (1) chronic health effects (carcinogenicity), (2) microbial recalcitrance, (3) high bioaccumulation potential, and (4) low removal efficiencies in traditional wastewater treatment processes (2). PAH compounds have been identified and summarized for a variety of domestic and industrial liquid wastes and solid residues (5,7,9). Based on a comprehensive review of the literature and laboratory treatability studies, Sims and Overcash (8) summarized the behavior and fate of PAH compounds in soil systems. The potential for effective treatment and safe ultimate disposal of PAH compounds is significant with regard to land treatment.

Recently promulgated hazardous waste land treatment regulations established by the U.S. Environmental Protection Agency (40 CFR section 264) requires a permit to operate a HWLT facility. Requirements specify that hazardous constituents contained in a waste to be land treated must be degraded, transformed, and/or immobilized in the soil treatment zone. A treatment demonstration must be conducted in order to specify design and management requirements including: (1) waste application rate, (2) waste applica-

tion frequency, (3) waste application method, (4) measures to control soil pH, (5) measures to increase microbial activity, (6) measures to increase chemical reaction, and (7) measures to control soil moisture.

PURPOSE

Research is needed to provide engineering design and management information for land treatment systems receiving wastes containing PAH constituents. Because of the diverse inputs of site characteristics, waste constituents, soil reactions, and assimilation capacities, development of a methodology for using information concerning the behavior and fate of PAH constituents in land treatment systems is required.

For this research effort, information was obtained concerning: (1) waste loading rates, (2) rates of degradation, (3) measures to increase microbial activity, and (4) mutagenic characteristics transformation for soil incubated priority pollutant PNA compounds. A protocol for obtaining this information was developed and evaluated. The three-step protocol included: (1) incubation, (2) characterization/ identification, and (3) determination of mutagenic potential. The protocol involved interfacing high performance liquid chromatography (HPLC) for compound and metabolite characterization with the Ames Salmonella typhimurium mammalian microsome mutagenicity assay for determination of genotoxic potential of PNA compounds and transformation products in soil.

APPROACH

Incubation

PNA compounds were incubated, singly or in a complex waste, in an environmentally controlled chamber in glass soil reactors. Environmental parameters that were controlled included temperature (25°C), light exposure (dark to prevent possible photodegradation, or light to encourage photodegradation), and soil moisture as percent field capacity.

Chemical Characterization with HPLC

Procedures for extraction and analysis of PAH compounds were based on the high performance liquid chromatography procedure for analysis of PAH compounds in water samples (4). HPLC was used with acetonitrile-water as the mobile phase, and a C-18 Perkin Elmer reverse phase column was used as the stationary phase. PAH compounds and metabolites were characterized with a UV detector at a wave length of 254 nm.

A subset of soil extracts was fractionated using a C-8 preparative Lobar size-A prepacked column. Polarity classes of degradation products were collected in acetonitrile-water, evaporated, and redissolved in dimethylsulfoxide for the Ames assay.

Mutagenicity Evaluation

The Ames *Salmonella typhimurium*/mammalian microsome mutagenicity assay (6) was used to determine the genotoxic potential of complex extracts (unfractionated) as well as parent compounds and biodegradation products obtained with the fractionation procedure described above.

Enhancement of Microbial Activity

Potential engineering management options for stimulating microbial activity include analog enrichment, complex substrate enrichment, nutrient addition, surfactant addition, pH adjustment, and moisture adjustment. The options may provide tools for increasing the rate of biodegradation of PAH constituents and therefore increasing the soil assimilative capacity for these constituents. Phenanthrene was used as an analog enrichment, at a concentration of 1000 mg/kg soil. Raw manure addition to soil reactors was the complex substrate enrichment and was calculated based on nutrient content. Nutrient addition including nitrogen and phosphorus was added as the salt solution recommended by Hoagland and Arnon (3). To investigate the effect of surfactant addition on the soil assimilative capacity for PNA constituents, Triton-100 surfactant was used at 2 ml/200 gm soil dry-weight. For pH adjustment, CaCO₃ was used to neutralize a Norfolk fine sandy loam (pH = 6.1); soil pH was adjusted to 7.0. The effect of soil moisture on PNA assimilation capacity was investigated with two soil moisture ranges, 20-40 percent field capacity and 60-80 percent field capacity.

Chemical and mutagenic data were subjected to analysis of variance, and when significant differences at the 5 percent level were found, Duncan's New Multiple Range Test was employed to separate means. The statistical procedures were performed using standard package programs of Statistical Analysis Systems-76 (1).

PROBLEMS ENCOUNTERED

One problem concerned the type of soil reactor/sampling approach used. Because of the difficulty of achieving completely homogeneous mixtures of soil and waste or soil and PNA compound, accurate reproducibility for results of subsampling soil from one reactor is difficult to achieve. Therefore, the entire contents of each glass soil reactor was used for each sampling event; replicate soil reactors were prepared in order to obtain samples through time. Triplicate reactors were used for each sampling event.

RESULTS

Based on a comprehensive review of the literature and on laboratory treatability studies, initial rates of transformation of PNA compounds in soil as a function of initial soil concentration based on first order kinetics are presented in Figure 1. These data were corrected for variation in temperature using an Arrhenius equation with coefficients developed from PNA data to a temperature of 20°C. Rates were normalized to micrograms PNA transformed per gram soil dry-weight per hour. The general trends shown in Figure 1 can be summarized as follows: (1) for a given PNA compound, the initial rate of degradation increases with increasing initial soil concentration, and (2) within the class of PNA compounds the initial rate of degradation decreases with increasing number of fused benzene rings (or molecular weight).

Results for PNA degradation kinetics from laboratory studies

and from the literature indicate that most PNAs have reasonable, finite half-lives in soil systems at the concentrations evaluated. Kinetics of degradation were found to be related to PNA structure. Arranging PNAs by number of rings indicates that there are distinct statistically different groups of PNA compounds. The range of half-lives is similar for low and high soil loadings (19-190 days) while the initial soil concentration varies over a range of 0.07 to 147 ppm (2000 fold). However the initial rate of degradation varies by a factor of 2500.

Results of experiments with engineering management options suggest that it may be possible to influence the degradation rates of PNA compounds. The effect of several amendments on the degradation of benz(a)pyrene is presented in Table 1. The degradation of B(a)P, a five ring PNA compound which is considered to be cometabolized, i.e., cannot serve as a source of carbon and energy for the growth of microorganisms, appears to be influenced by pH adjustment and analog enrichment. Statistical analysis of the data indicated significant differences among the treatments, as shown in Table 1.

The effects of simultaneous addition of a complex substrate amendment, raw manure, and pH adjustment on degradation kinetics for a complex waste containing PAH compounds is presented in Table 2. Manure provided an inoculum of microorganisms and degradable organic carbon sources for soil microorganisms. pH of the waste: soil mixture was adjusted from 6.1 to 7.5. Results are presented for

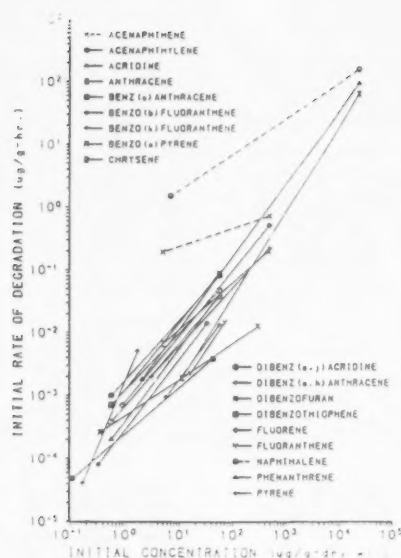


Figure 1. Rates of Transformation of PNA Compounds in Soil as a Function of Initial Soil concentrations.

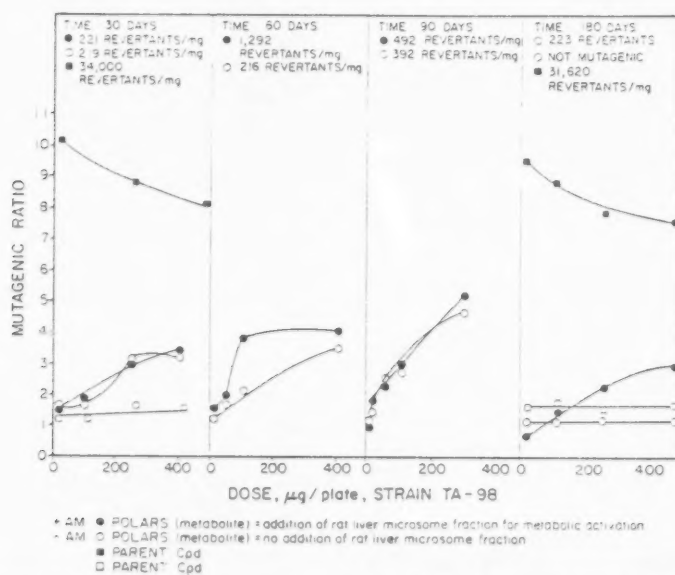


Figure 2. Mutagenicity of soil incubated B(a)P and metabolites (7).

PAH compounds identified and quantified in waste:soil mixtures without and with the amendment described.

Results presented in Table 2 indicate that degradation of all PAH compounds was affected by the amendments. PAH half-lives were greatly reduced compared with half-lives in unamended soil.

Table 1. Effect of amendments on benz(a)pyrene degradation.

Treatment	Half-life (days)
None	90 A ^a
Nutrients	81 A
pH Adjustment (5.2 to 7.4)	64 B
Surfactant	87 A
Analog enrichment with phenanthrene	64 B

^aValues are means of three replicates. Means followed by same letter are not significant at the 0.05 level.

The effects of moisture amendment on the degradation of pure PAH compounds applied to soil batch reactors is presented in Table 3. For all three PAH compounds evaluated, degradation rates were improved by adjustment of soil moisture from 20-40 percent of field capacity to 60-80 percent. Thus results for amendment additions to PAH compounds present as individual constituents or in complex waste in soil indicate that management techniques are available for optimizing degradation kinetics.

Intermediate products formed in the degradation of PAH compounds in soil systems, as a class, proceed through a cycle of generation and degradation which complements the parent compound cycle in soil. Intermediate degradation products are generally more polar than parent PAH compounds (8), and thus are more readily transported (leached) through soil systems than parent PAH compounds. Optimization of treatment of PAH compounds, therefore,

Table 2. Effect of manure and pH amendments on PAH degradation in a complex waste incorporated into soil.

PAH Compound	Half-Life in Waste:Soil Mixture (days)	
	Without amendments	With amendments
Acenaphthylene	78	14
Acenaphthene	96	45
Fluorene	64	39
Phenanthrene	69	23
Anthracene	28	17
Fluoranthene	104	29
Pyrene	73	27
Benz(a)anthracene	123	52
Chrysene	70	42
Benzo(b)fluoranthene	85	65
Benzo(k)fluoranthene	143	74
Benzo(a)pyrene	91	69
Benzo(ghi)perylene	74	42
Dibenz(a,h)anthracene	179	70
Indeno(1,2,3-cd)pyrene	57	42

Table 3. Effect of soil moisture on PAH degradation (results presented as half-life in days).

Moisture	Anthracene	Phenanthrene	Fluoranthene
20-40% field capacity	43	61	559
60-80% field capacity	37	54	231

also requires optimizing treatment of PAH degradation products.

The Ames assay was used to determine the mutagenic potential of PAH degradation products in soil. Figure 2 presents results of laboratory studies with the PAH compound B(a)P and soil metabolites of B(a)P. It is obvious from Figure 2 that the mutagenicity of polar degradation products increases and then decreases with incubation time, or treatment time, in soil. Results also indicate that the mutagenic potential of degradation products, as a class of polar metabolites, is much less than the parent compound. A detoxication pathway is indicated for soil biodegradation (Figure 2).

The Ames assay was also used to evaluate potential mutagenicity of leachates produced in glass column leaching experiments conducted with complex wastes containing PAH compounds. Results for the Ames testing of leachates are summarized in Table 4. Results for the control leachate collected from columns without waste addition demonstrate a negative response

Table 4. Results for Ames assay testing of leachates. (Results expressed in terms of mutagenic ratio. Negative response indicated by mutagenic ratio of less than 2.0).

Treatment	Treatment Time (days)		
	0	61	91
Control ^a	1.50	1.75	1.50
Waste:Soil Mixture	1.25	4.05	1.85

^aControl indicates soil only (no waste addition).

(mutagenic ratio is less than 2.0), and therefore the leachate from soil with no complex waste addition is not mutagenic.

Results for leachate generated at the beginning of the study for the waste:soil mixture also demonstrated no mutagenicity. This result is expected since the parent PAH compounds are not highly soluble in water. PAH compounds also demonstrate high partitioning into soil organic matter (8), and the soil used in the laboratory study had a relatively high organic carbon content of 1.0 percent. Also very few PAH degradation products would be expected immediately after waste incorporation into soil.

Results for leachate generated at 61 and 91 days after initial waste incorporation into soil indicate increased mutagenicity (intoxication) followed by decreased mutagenicity (detoxication) compared with the initial waste incorporated soil. Thus polar metabolites resulting from PAH degradation in

soil are mutagenic and may be transported through soil under saturated conditions. More research is required to characterize the mobility and toxicity of biodegradation products of PAH compounds in soil systems.

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Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

A NEW VENTURE IN INTERNATIONAL WASTE MANAGEMENT

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ABSTRACT

The paper discusses developments in waste management possibilities, technologies, services and institutions that are opened up by international transfer. It is demonstrated that, under careful management, the international transfer either of wastes or experience can benefit the United States both in the short and long term in its continuing search for radically improved hazardous waste management.

Disclaimer

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THE UNITED STATES/MEXICO ENVIRONMENTAL AGREEMENT OF 1983
BI-NATIONAL HAZARDOUS MATERIALS & WASTE MANAGEMENT

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ABSTRACT

The Agreement between the United States of America and the United Mexican States on Cooperation for the Protection and Improvement of the Environment in the Border Area was signed by Presidents Reagan and de la Madrid in La Paz, Mexico on August 14, 1983. It reaffirms, through political will, the great importance each nation places on a healthful common environment and demonstrates a commitment to cooperatively solve environmental problems of mutual concern in the border area. The Agreement also requires that each nation facilitate the prevention, reduction, and elimination of sources of pollution within its purview which may affect the neighboring country.

The US Environmental Protection Agency (EPA) and Mexico's Subsecretariat de Desarrollo Urbano y Ecologia (SEDUE) were designated as National Coordinators to implement the Agreement. The National Coordinators established three bi-national technical teams - one focusing on air pollution, one on water pollution and one which is the subject of this paper, the US/Mexican Hazardous Materials and Waste Management Workgroup. The Workgroup was charged with identifying and addressing actual or potential hazardous material and waste management problems of mutual concern to the border area.

The Workgroup identified 7 areas for priority action and developed specific short and long term objectives to address each problem area. These areas are: the transboundary movement of hazardous materials, joint inland contingency response planning, training, agricultural chemicals, in-bond companies, municipal and hazardous waste facilities, and ocean incineration.

Workgroup efforts to prevent, eliminate and reduce border pollution problems involving hazardous materials and waste can best be accomplished when primary bi-national relations are harmonious, where cooperation and responsiveness distinguish local as well as federal interactions and where there is a sufficient commitment of staff and resources. The cooperation of the generators, transporters and disposers of hazardous materials and waste through compliance with EPA and SEDUE regulations and policies is essential.

INTRODUCTION AND PURPOSE

On August 14, 1983 Presi-

dents Reagan and de la Madrid signed the "Agreement between the United States of America



A detailed map of the Rio Grande border region. The map shows the following states and territories: CALIFORNIA, ARIZONA, NEW MEXICO, TEXAS, CHIHUAHUA, and SONORA. Major cities and towns labeled include San Diego, El Paso, Juarez, Laredo, Brownsville, McAllen, and Bixby. Rivers shown include the Colorado River, Sacramento River, San Pedro River, and Rio Grande. The map also depicts the Gulf of California (Golfo de California) and the Gulf of Mexico (Golfo de Mexico). A scale bar indicates distances in miles (0 to 100) and kilometers (0 to 160). The map is dated 'L. Raini 1985'.

and the United Mexican States for the Protection and Improvement of the Environment in the Border Area." The Agreement established a 200 km wide zone of mutual interest along the border, covered all environmental media and designated the United States Environmental Protection Agency (EPA) and the United Mexican States' Subsecretariat de Desarrollo Urbano y Ecologia (SEDUE) as the National Coordinators to implement the Agreement. On March 8-9, 1984 EPA and SEDUE delegates convened in Tijuana, Mexico and San Diego, CA to discuss common interests and concerns in the areas of air, water, and soil pollution (issues involving toxic substances and hazardous waste management were initially included within the category of "soil pollution"). To initiate cooperative measures within the framework of the Agreement, the delegations established three bi-national technical workgroups: air, water, and soil.

This paper chronicles the developments of the technical workgroup on soil now called the US/Mexican Hazardous Materials and Waste Management Workgroup, and discusses the current status and future expectations of US/Mexican hazardous materials and waste management.

It is hoped that the subject information will inform those parties in the public, private and academic sectors with interests particular to US/Mexican hazardous materials and waste management.

US/MEXICAN BORDER ENVIRONMENT

The US/Mexican border is approximately 1900 miles long, of which 1230 miles is largely the Rio Grande River. The Border begins and ends with the Pacific Ocean on the west and the Gulf of Mexico on the East. Several surface waterways transect the border: the Tijuana, Alamo, New, Colorado, Santa Cruz, and San Pedro Rivers. The Salton Sea, Laguna Salada, Greenbrush Draw, Nogales Wash and the Gulf of California are significant water basin features either partially or fully located within the border area.

Land and water uses in the border area include some of the most productive agricultural and ranching lands in the US and Mexico, commercial fishing, mining and minerals processing, nuclear power generation and increasing industrialization and associated urbanization.

Documented environmental issues in the border area include air quality, water quantity and quality, marine pollution, soil contamination, and wildlife habitat destruction.

WORKGROUP ORGANIZATION

There are four states on the US side of the border: two in EPA Region 9 - California and Arizona and, two in EPA Region 6 New Mexico and Texas.

The US Workgroup delegation chaired by the Director of the Toxics & Waste Management Division, EPA Region 9

and consists of four EPA officials from Regions 6 and 9 and the Office of International Activities (OIA) and one US Embassy official.

There are six states on the Mexican side of the border: Baja California, Sonora, Chihuahua, Nuevo Leon, and Tamaulipas. The Mexican Workgroup delegation, chaired by the SEDUE Director of the Prevention and Control of Environmental Contamination, consists of four SEDUE officials and is based in Mexico City.

WORKGROUP GOALS AND OBJECTIVES

To best clarify the problem field of the Workgroup - hazardous materials and waste - the Workgroup first proposed that its name be changed to the Hazardous Materials and Waste Management Workgroup. The original name, the Soils Workgroup, was determined to be inappropriate because it implied that the Group was concerned with one of the pathways of contamination (soil) instead of proper management of the substances of contamination.

The longterm goal of the Work group is to identify and address as appropriate, actual or potential hazardous material and waste management problems of mutual concern along the US/Mexican border.

7 problem areas of mutual concern were identified as requiring priority action and subdivided into primary and secondary issues:

Primary Priority Issues

The Transboundary Movement of Hazardous Materials

Joint Inland Contingency Planning

Training (Note: To highlight the importance of this primary priority area, a specific objective of the Workgroup's long term goal is the professional development of individuals to enhance the capability to address hazardous material and waste management issues.)

Secondary Priority Issues

Agricultural Chemicals

In-Bond Companies

Municipal and Hazardous Waste Facilities

Ocean Incineration

THE TRANSBOUNDARY MOVEMENT OF HAZARDOUS MATERIALS

Current US and Mexican efforts have been inadequate to prevent the indiscriminate and uncontrolled transborder movement of hazardous materials.

US legislation that addresses hazardous waste exports is contained within Section 245 of the Resource Conservation and Recovery Act (RCRA) ammended in November, 1984.

Currently, even those exporters of "RCRA regulated" hazardous waste are only required to notify* OIA with 30

days anticipation of their first export of the year, so that OIA may notify the recipient country's government. Approval from the foreign government is not requested. However, commencing in November, 1986, RCRA will require that no person may export hazardous unless: 1) they have filed a notification with EPA's OIA and, 2) the receiving country has agreed in writing to accept the waste and, 3) a copy of the acceptance is attached to the manifest.

Additionally, an annual report** must be filed with OIA for each preceeding calendar year's activities.

RCRA does not fully regulate exports of material claimed to be "product" or for reuse, nor of low volume waste shipments. If the exporters and transporters characterize the material in ways that exempt the shipment from RCRA regulation, appropriate communication of the transboundary movement may not be achieved.

Workgroup objectives for this priority issue are: Short Term 1) to develop a system to communicate information concerning transborder movements, 2) establish a direct EPA to SEDUE Regional Hot Line to communicate information on known and potential shipments and; Long term 1) to develop a mechanism to implement the new RCRA legislation through a Bi-national Agreement, 2) to investigate "sham recycling", and 3) to assess the need for statutory/regulatory changes based upon ongoing Workgroup efforts.

Specific short term Workgroup activities underway to address this priority issue include sharing all available information on hazardous materia imports, developing an ongoing training program for US and Mexican Custom Agencies in the area of transborder hazardous material movement and, increasing surveil lance to identify potential illegal imports and exports.

* The exporter(generator) must file a notification only once per calendar year with an estimate of the waste type and quantity, the frequency, dates and ports of entry, method of transportation, treatment, storage, and disposal, and the name/location of the foreign consignee.

** The annual report must summarize the types, quantities, frequencies, and ultimate destination of all hazardous waste exported during the previous year.

JOINT INLAND CONTINGENCY PLANNING

In July, 1980, an oil spill response agreement, titled, the "Agreement of Coordination Between the United States of America and the United Mexican States Regarding Pollution of the Marine Environment by Discharges of Hydrocarbons and Other Hazardous Substances," was signed.

A Contingency Plan to be implemented by the US Coast Guard and the Mexican Navy was

developed as a series of annexes to the Agreement and outlines cooperative measures and procedures to be taken in the event of a discharge to the marine environment. This Marine Plan served as the model for an EPA Headquarters drafted document which was submitted to SEDUE for approval as an Annex to the US/Mexican Environmental Agreement.

In May, 1985, the Workgroup convened in San Francisco to discuss the still unsigned Plan as a Workgroup agenda item. Through technical discussions and negotiations and increasing familiarity with each other's needs, abilities, limitations and potentials, the Workgroup revised the Plan and jointly endorsed it for recommendation to the National Coordinators. This Agreement and its set of appendices is called "The Agreement of Cooperation Between the United States of American and the United Mexican States Regarding Pollution of the Environment Along the Inland International Boundary by Discharges of Hazardous Substances," or The Plan.

Plan Objectives

The primary intent of the Plan is to provide for a coordinated response capability at the scene of a discharge of hazardous substances that pose or may pose a threat to the public health, welfare or the environment. Apart from joint response authority, the Plan commits each country to provide contingency planning within its own boundary.*

The Plan calls for a Joint Response Team (JRT) to be headed by US and Mexican Co-Chairmen. As required by the Plan and via the JRT, bi-national agreement will be necessary to initiate a joint response, to determine what response measures will be taken and when to terminate the response.

The Plan outlines the designation, functions and responsibilities of the JRT and primary response officials such as the On-Scene Coordinator (OSC) and the Advisory Liaison Coordinator (ALC).

Workgroup objectives for this priority issue are: Short Term 1) Signature of the Plan and, 2) Development of an implementation plan with a schedule and list of participants, and; Long Term 1) Full implementation of the Plan and, 2) A joint emergency response exercise.

Specific short term Workgroup activities underway to address this priority issue include developing local response plans involving sister cities.

The Workgroup will facilitate a pilot program for the city pair of Mexicali/Calexico.

The pilot will help develop model procedures for notification and response.

Under its responsibility to implement the National Contingency Plan (NCP), EPA recognized that area specific border contingency planning was needed to complement existing contingency plans.

Prior to the initial Workgroup meeting, EPA contacted local, state, county, regional, federal and academic parties with interests, responsibilities, experience and expertise specific to hazardous material issues in the border area. A resultant document outlined border agency authorities, concerns (both known and potential) and abilities to participate in Workgroup and/or response activities. Regional Border Task Forces were then created to facilitate information flow and response capabilities.

* The US' National Contingency Plan (NCP) (with Regional and Local subsets) provides for response to emergencies caused by oil spills and releases of hazardous substances to all media (land, air, surface water and ground water).

TRAINING

Recognizing that resolving environmental problems requires educating and properly equipping those persons who will participate in accomplishing Workgroup objectives, the issue of training is of highest priority.

Workgroup objectives for this issue are: Short Term
1) Comprehensive assessment of training needs and; Long Term
1) Development and implementation of a permanent and formal training program.

Specific short term Workgroup activities planned to address this priority include:
1) EPA will inform SEDUE of

response activity to be held in the border area so that SEDUE may send site observers;
2) SEDUE is expected to provide EPA with an assessment of their training needs;
3) EPA will provide SEDUE with available training options;
4) The Workgroup will establish workshops and explore bi-lateral personnel assignments to address specific training needs.

SECONDARY PRIORITY ISSUES

Agricultural Chemicals
In-Bond Companies
Municipal and Hazardous Waste Facilities
Ocean Incineration

It was agreed that the Workgroup did not possess enough information on these issues or their environmental/public health impacts to identify specific implementation actions to address them. Therefore, these secondary issues of mutual concern will be elevated to primary issues if additional data and problem assessment indicate the need to do so.

Workgroup objectives for these issues then, focus on the generation and communication of information: 1) Identification and exchange of environmental data; 2) Exchange of technical information and; 3) Notification of any significant actions or events.

Workgroup activities inspired by the Municipal and Hazardous Activities Issue include:
1) EPA has provided SEDUE with hazardous waste land disposal technical manuals and, 2) EPA held technical briefings and

hosted a tour of several US hazardous waste land disposal sites for a delegation of SEDUE and Mexican industry officials during May, 1985.

CONCLUSION

- * There are dramatic environmental and health consequences possible due to the improper handling of hazardous materials.
- * The Workgroup is in its beginning stages of problem assessment.
- * There is insufficient information on the extent of US/Mexican hazardous materials and waste problems in the border area.
- * In order to meet present and future requirements for effective and safe transborder hazardous material and waste management will depend upon the development of:
 - An effective system of identification and evaluation of hazardous materials.
 - Positive efforts in the fields of research and science, industry and appropriate technology, cross cultural implementation, international peace and harmony, legislative and diplomatic mechanisms, cooperative enforcement, and the generation and appropriate application of reliable information.

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

MANAGEMENT OF HAZARDOUS WASTES GENERATED BY
CHEMICAL INDUSTRIES IN INDIA

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ABSTRACT

Hazardous Waste Management has so far received perfunctory attention in India. Quantitative information on a countrywide basis concerning the nature and quantities of hazardous wastes from chemical industries is not available. A sample survey, commissioned by the Department of Environment, on selected chemical industries has revealed that as much as 22 percent of solid wastes are hazardous in nature. These are usually disposed in nearby, lowlying areas without proper treatment and protection measures. India's current laws and regulations do not adequately provide for safe handling and secured disposal of hazardous substances. An appropriate Act and institutional mechanism must be instituted to regulate disposal of these substances. Some steps that have recently been taken include industrial location policy, procedure of environmental clearance for project approval, formulation of industry-specific standards, and fiscal incentives for pollution control. An integrated approach in terms of policy and regulatory and promotional measures is recommended for coping with the mounting problems of hazardous waste management.

Disclaimer

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THE BAVARIAN SYSTEM FOR SPECIAL WASTE MANAGEMENT -
15 YEARS EXPERIENCE IN COLLECTION, TREATMENT,
DISPOSAL AND CONTROL

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ABSTRACT

Bavaria with an area of 70 000 sq.kms and nearly 11 millions inhabitants was the first State in the Federal Republic of Germany (FRG) to address central responsibility for the disposal of special wastes. In the middle part of the State, a regional special association was formed in 1966 to operate waste disposal sites ("Zweckverband Sondermüllplätze Mittelfranken", abbreviated as "ZVSMM"). Soon thereafter the Bavarian Corporation for Disposal of Special Wastes, Ltd. ("Gesellschaft zur Beseitigung von Sondermüll in Bayern mbH", abbreviated usually as "GSB") was established in 1970 to provide and operate facilities necessary for the proper management of industrial wastes. The GSB operates a network of regional collecting points and several central disposal facilities. At present in Bavaria 10 regional collecting points and 3 central special-waste disposal facilities are in operation, in which nearly 350 000 tons special waste are treated and disposed per year.

The special waste is temporarily deposited at the collecting points, where it is classified for bulk transport to the disposal plants. In addition, the collecting points are responsible for pretreating waste like neutralisation, dewatering, emulsion separation and sludge thickening.

The central disposal facilities in Ebenhausen (near Ingolstadt) and Schwabach (near Nürnberg) are one of the most advanced of its kind in the FRG and consists central laboratories, chemical-physical treatment, incineration (rotary kilns) and secure land-fill sites. The Landfill Gallenbach, in operation since 1975 will also discussed in this paper in view of collection, analysis and treatment of leachate. A research program had been undertaken for treating the leachate in a distillation plant.

Since 1972, GSB runs also a recycling plant for contaminated solvents with a capacity of 4000 tons per year.

INTRODUCTION

The FRG was one of the first European countries to give serious attention to the problem of hazardous waste. It passed the Waste Disposal Act in 1972. The Federal Government has some responsibility for managing hazardous waste. There is national legislation and international issues are a federal concern. However, the Landers or States have the legal responsibility for implementing and enforcing the legislation. At the national level, the German Ministry of Interior published a list of about 570 types of waste in 1975 and two years later 38 waste streams were identified as special or hazardous. These substances are defined by category (e.g., gas scrubber sludges), technology (e.g., electroplating), general grouping (pesticides) or specific proscription. About three to four million tons of hazardous waste are generated each year in the FRG. About 50 percent is disposed of in secure land-fill sites, 35 percent is treated by chemo-physical means and the final 15 percent is disposed off by incineration.

Within the system of waste treatment in the State of Bavaria there has developed an elaborate charge system during its 15 years of operation.

Wastes usually are delivered to the ten collection stations situated around Bavaria (see Figure 1) by the waste generators. Preliminary treatment of

some waste takes place at these collection stations and then the waste is transported by private carriers to the three major disposal sites in the state. There the wastes are treated in a manner designed to remove the hazard from wastes by an overall cost minimizing technology.

APPROACH

Company for Disposal of Special Waste ltd. (GSB)

With the exception of the treatment plant of Schwabach which is run by a municipal co-operative, called "Zweckverband Sondermüllplätze Mittelfranken" (ZVSMM), all the other facilities and collecting stations are run by the "Gesellschaft zur Beseitigung von Sondermüll in Bayern mbH" (Company for Disposal of Special Waste in Bavaria ltd.), for short "GSB", which was established as a country-wide organization in 1970. It's stock fund amounts arose from 1 million in 1970 to 21 millions DM today. Shareholders of the company are the Bavarian State (78 %), 3 municipal organizations (8 %) and 76 industrial firms (14 %). The task of the GSB is to provide and operate facilities necessary for the treatment of special waste and the recovery of raw materials from special waste all over Bavaria. The activity of the company is conducted on a not profit-base but being a private company the GSB has to search permanently new ways to treat the hazardous waste in order to get a proper

Figure 1



- 10 collecting points
- 3 central treatment and disposal facilities (incineration, chemo-physical treatment, landfill)
- 1 recovery plant for contaminated solvents

disposal or a recovery of raw materials from this waste.

Since GSB waste disposal is not profit oriented and since the board of directors, which represents the shareholders, must authorize the disposal costs, the conditions have been created under which industrial and manufacturing establishments deliver their wastes for orderly treatment in accordance with the law but without having to be forced (court orders, fines). The publicly held share of over 75 % in the company guarantees optimal environmental protection being the first priority during construction and operation of all facilities and also in the choice of methods used in waste disposal. The GSB has served as the model for similar corporate entities with identical tasks in other States of the FRG.

Collection and Transportation

The collecting points are fairly uniform in the service and in their equipment (see Figure 1). They provide an intermediate holding function and have equipment, which is fairly simple to run. They pretreat as much waste as possible to cut down the volume. They have a waste water treatment plant, in which the separation of the usually large volumes of oil-water mixtures into water and solids takes place. The treated waste-water is discharged locally. The waste volume is cut back to 10 % of the original. Where necessary,

facilities for neutralizing and sludge thickening are in place. All gathering points have an administration building and testlab, vehicle scales and an area for oily soil and containers to receive and provide intermediate storage for industrial sludges of all types.

Ebenhausen central treatment facility

The biggest and most modern of the three bavarian hazardous waste facilities is the facility Ebenhausen which started up 1976 on a 4 hectare site in Ebenhausen near Ingolstadt and a 17 hectare landfill in Galtenbach 25 miles away (no suitable site was available next to the treatment plant Ebenhausen). The Ebenhausen plant comprises a laboratory, a chemical-physical treatment plant for organic and inorganic substances (oil-emulsions, used acids, alkalies, galvanizing and other inorganic sludges, solutions containing chrome, cyanides, nitrites etc.), a water purification plant, as well as Germany's largest waste incineration plant with a capacity of 100 times 10 to the sixth power btu/h or 70 000 tons (see Figure 2).

Incineration

The incineration plant, able to process 70 000 tons/yr waste, has two parallel rotary kilns for solid and pasty wastes and a common burner-chamber with a set of six burners for liquid wastes. The heat of the off-gases from the after-burners is utilized in a steam boiler

where the off-gases are cooled down from 1 000 centigrades to about 270 centigrades, thereby generating up to 30 tons steam/h out of which 22 tons/h are consumed in a 1,530 kw steam turbine while the remainder is condensed in an air condenser; this electric energy not only the incineration plants entire power requirement but actually leaves an excess supply for the public grid. The steam from the turbine (three atmospheres pressure) is utilized for heating the building and for process heat in the chemical-physical treatment plant.

Off-gas purification comprises an electrical precipitator for dust retention and a two-stage venturi-type scrubber which removes HCL and HF almost completely while retention of SO₂ is 70 pc. is enhanced by flocculants. As regards airborne emissions and scrubbing water pollutants, this industrial incinerator has been reviewed several times. From simultaneously performed measurements of HCL, SO₂, HF and dust in raw gas and clean gas, the following fluctuation margins for routine operation can be derived:

Pollutant	Raw gas mlg/m ³	Clean gas mg/m ³	limit mg/m ³
HCL	1000-4000	22-90	100
SO ₂	450-2100	40-300	400
HF	62-260	1-3	5
dust	1000-2000	10-20	50

Table 1
Emission rates of the
Ebenhausen incineration

Chemical-physical treatment

In the physicochemical treatment plant the materials are enloaded in one of the different 30 m³ receiving tanks depending on the results of the laboratory tests. These tanks lead into several storage and finally, there are followed by the individual treatment facilities of mixing and dosing units.

Liquids with inorganic and organic contaminants are treated in the following way:

- neutralizing
- detoxification
 - o oxidation cyanid
 - o oxidation nitrite
 - o reduction chromate
- Separation of solid substances (decanter)
- Chemical separation of emulsions
- Flocculation of oil
- Precipitation of metal salts
- Flocculation, using polyelectrolytes
- Separation of sludge and water phase (in drum filters)
- Subsequent treatment, employing oxidation and reduction processes

The residues of the treatment processes (dewatered, neutralized sludges, fly-ash, slag) and other solid wastes are deposited at the two landfill sites in Schwabach and Gallenbach by special security conditions. A third landfill site, located in Raindorf goes in operation in June, 1985, and will be the most modern site

in Europe (capacity: 800 000 m³, basic-clay-cover: 2.0 m, owner: ZVSMM). While the landfill site of Schwabach is located together with the treatment facilities, the Gallenbach site is dislocated (over 40 km) from the Ebenhausen treatment facilities in view of hydrogeological conditions.

Gallenbach Landfill

The Gallenbach Landfill is in operation since 1975 and comprises the following installations: (see Figure 3)

- Operational building with amenity rooms of various types for the personal.
- Laboratory for sampling of the substances delivered.
- Vehicle weigh bridge.
- Vehicle and instrument shop.
- Control systems (drainage, retaining basins) for holding and treating the storm water and leachate.

The site is operated by the 'area method' of landfilling on a 100 cm thick, pre-constructed clay pad with a reported permeability of 10^{-8} m/s. Watersoluble solid wastes containing heavy metals are desposited in drums and covered with concrete to reduce the contamination in the leachate.

In addition to daily cover, a plastic membrane is intermittently placed over completed lifts to reduce infiltration. A hand operated vibrator is also utilized to

compact daily cover in an effort to reduce the volume of leachate generated. The quantity of leachate could be reduced in the last years through several measures like high compaction, applying layers of impermeable material, landfilling in small sections from 80 % to nearly 40 %.

Collection, Characteristics and Treatment of Leachate

Leachate is collected by a series of underdrains, located in the clay pad. Leachate is then channeled to a plastic lined (3 mm) detention pond from where it is trucked to Ebenhausen-Plant for treatment. Approximately 10,000 tonnes per year of leachate is hauled 40 km to the Ebenhausen complex. Average leachate characteristics are identified in Table 2.

Parameters	1977	1978	1979	1980	1981	1982	1983
pH	7,0	7,4	7,2	7,4	7,4	7,5	7,6
BOD ₅	2720	3000	4000	4650	4370	3500	2500
COD ₅	3000	3500	9000	12000	-	-	3600
TOC	1600	1900	4000	3400	3700	3100	1700
Cr	0,4	0,7	0,5	0,2	1,0	0,5	0,3
Cu	0,3	0,3	0,4	0,3	0,4	0,3	0,1
Cn	-	-	0,1	0,1	0,1	0,1	0,1
Ni	4,1	5,2	3,6	4,4	4,1	4,1	2,5
Zn	2,3	0,5	0,6	0,4	0,7	0,6	0,7
Cd	0,2	0,1	0,2	0,2	0,8	0,2	0,1
Fe	12	4	4	2,1	2,7	3,5	1,7
Sn	2,3	8	44	34	3,1	3	2
Pb	0,6	1,0	1,2	1,1	6,4	1,8	0,6
Phenole	2,1	7,3	1,0	10	14	8,6	12
Choloride	15000	26000	37000	40000	51000	44000	28000
Sulphate	21	3400	8300	3300	4100	1700	3800
Amonia	118	433	900	900	920	1000	790

Table 2 : Average leachate concentrations (mg/l) in Gallenbach
1977-1983

The leachate is characterized by high organic (BOD, COD, TOC) and inorganic concentrations, in particular salt contents between 15 g/l and 50 g/l and ammonia between 100 mg/l and 1000 mg/l also some heavy metals like zinn with 40 mg/l.

From nearly 84 000 m³ leachate, generated 1976-1982, it was estimated that over 3260 metric tons were produced as salt and about 2750 kg heavy metal ions were diluted. In relation of the landfilled quantity of solid wastes (480.000 t) during 1976-1982 only 0,7 % of this material had been diluted.

In view of the high contamination of the leachate it can't be discharged into the receiving stream, the Paar, a tributary of the Danube, so it has to be pumped from the retaining basin into lorry and after 40 km-transport treated in the chemo-physical plant and sewage plant in Ebenhausen. Task of the treatment is the reduction of the heavy-metal-content of the leachate by precipitation and changing pH-values.

The conventional treatment makes clear that several contaminants can't be reduced in a biological way or eliminated in common oxidation processes (high salt content, COD).

Therefore, on behave of the Bavarian Ministry of Environment a research program was undertaken for treating the leachate by a 2-stage distillation pilot plant in Ebenhausen. In the first step (acid distillation) the contaminants were cristalized and reduced in a salt concentrate. In the second step (alkaline distillation), the acid contaminants could be reduced again. The results made clear that TOC and COD could be reduced over 90 %, particularly by using the discontinuos distillation (reduction nearly 96 %).

Experience was made, that distillation of leachate can be a reasonable alternative to the conventional treatment. So the first distillation for up-scale plant in the FRG will go in 1986 in operation at the Schwabach Facility.

The Charges system and Investments

The disposal costs in Bavaria are reasonable, probably reflecting the facts that initial capital investments are not being amortized and that later capital investments are subsidized through interest-free or low-interests loans. The pricing formulas are quite involved and are summarized as follow. Waste treatment charges are established by process for each of the processes used in the major waste categories. The charges are designed roughly to cover the transportation from the collection centres

and the cost of waste treatment for each process.

Average treatment charges per ton (German Marks)

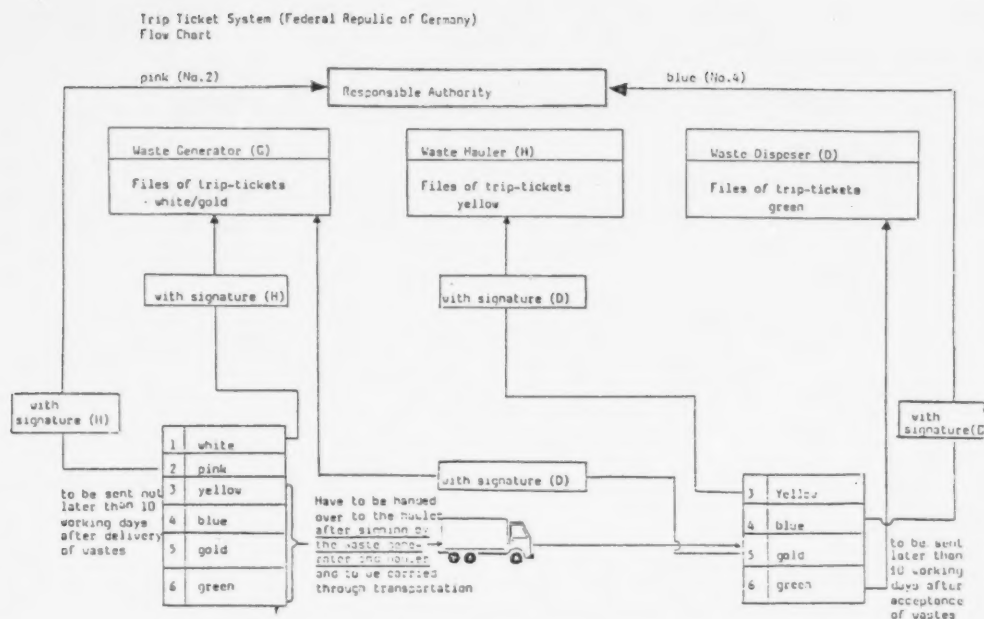
landfilling	DM 75,- - 190,-	(deposition in concrete jacket)
chemo-physical	DM 120,- - 300,-	
incineration	DM 325,- 1500,-	(PCB)

The hazardous waste disposal facilities in Bavaria required an investment of DM 120 million in the last 15 years. Financing is handled through subsidies, government loans and favorable interest terms (DM 70 million) and the company's own recources obtained by economic activity.

CONTROL

The FRG has a control system in which hazardous waste generators can and usually are required to initiate a trip-ticket, cradle-to-grave recording system of special waste involving six separate copies. Waste haulers, waste disposers and responsible agencies receive and/or transmit appropriate copies. Thus there are numerous places for cross-checking the kinds and quantities of waste as it travels to its final destination (see Figure 4).

In Bavaria, nearly 150 000 trip-tickets are controlled by the Bav. Environmental Protection Agency with the help of a computerized system.



Begleitschein Bezug zum Nachweis der Beseitigung von Abfällen
Dieser Begleitschein ist mit Unterschrift des Beförderers
im Nachweisbuch des Abfallerzeugers abzugeben

Nr.: 16 00057370

Type of Wastes		LAGA Waste Number	Waste Quantity
Consistency: fest = 1, flüssig = 2, gasförmig/schmelzschmelz = 3, steinartig = 4, flüssig = 5			
Vehicle License Number		Type of Vehicle	
Generator's No.		Transporter's No.	Disposer's No.
Name and Address		Name and Address	Name and Address
Date of Preparation		Date of Acceptance	Date of Acceptance
Versicherung der richtigen Beseitigung		Versicherung der ordnungsgemäßen Beförderung	Versicherung der ordnungsgemäßen Beseitigung

German Special Waste Manifest

Figure 4: Trip Ticket System in the FRG

Disclaimer

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HAZARDOUS WASTE COLLECTING AND TREATMENT IN AUSTRIA

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ABSTRACT

According to the new Federal Hazardous Waste Act that came into force in 1984, all hazardous and toxic substances must be collected and treated respectively disposed in proper facilities. Depending on the quantity and quality of waste there are several collecting and hauling systems available. In the near future there will be a network of collecting and transfer stations in the Austrian Provinces, whereas the Siggerwiesen/Salzburg plant with the annual capacity of 20 000 tons is representative. Most of the hazardous waste is shipped by rail or road to the central treatment plant EBS in Vienna. In the City of Vienna there is a chemical-physical treatment plant and a hazardous waste incineration plant with a total capacity of 160 000 tons annually. The excess heat is used to produce electricity and steam for the central heating system of the city. Due to the new federal Air Pollution Standard that came into force in 1984 additional flue gas cleaning devices must be installed, whereby new technologies are under consideration.

INTRODUCTION AND PURPOSE

The purpose of the paper is to demonstrate the efforts Austria is undertaking to improve its environment. The new Hazardous Waste Act as well as other new laws, regulations and standards require the improvement of existing treatment and disposal systems and the development of new technologies.

APPROACH AND PROBLEMS ENCOUNTERED

In Austria there are approximately 400 000 people employed in activities that generate hazardous waste. Assuming a specific amount of 280 kg per employee and year, the total quantity of hazardous and toxic waste results in 112 000 tons annually. Adding other commercial and industrial residues such as oil contaminated liquids and solids, other hydrocarbonic pollutants, etc. the total estimated amount of hazardous waste is 350 000 tons (t/a).

Table 1. ESTIMATED HAZARDOUS WASTE
GENERATED IN AUSTRIA

	t/a
hazardous waste	350 000
hazardous and toxic waste	112 000
specific quantity per employee	0,28
recommended treatment:	
incineration	105 000
physical-chemical treatment (CP-plant)	140 000
hazardous waste landfill	105 000

In Austria there are large quantities of industrial waste not classified at present as hazardous waste such as ashes and slag from coal fired boilers and steel mills. These wastes amount to several million tons annually and are landfilled in more or less controlled ways.

The Austrian Standard ÖNORM S 2100, Catalogue for Special and Hazardous Waste, describes more than 400 classes of substances. Each class and group has a separate code number, which is also used in the European common market. The standard ÖNORM S 2101, Hazardous Waste Requiring Supervision, contain 144 different hazardous substances in 12 groups. All substances mentioned in this catalogue must be declared by the owner or generator and be disposed by an authorized company.

Code No.	Substance
13	animal and slaughterhouse waste
31	inorganic waste
35	metal waste
51	oxides, hydroxides, salts
52	acids, alkaline solutions, concentrates
53	herbicides, pesticides

continue:

	and pharmaceuticals
54	mineral oil wastes
55	organic solvents, paints, adhesives, sealings, wax
57	plastic and rubber waste
58	textile waste
59	chemical waste
97	hospital waste

Beside all legal and administrative problems with the new regulations, there is also a lack of proper hazardous waste collecting and disposal facilities. The few existing plants must be extended and adapted to the increased environmental requirements. The air pollution requirements are much more stringent than before.

Table 2. EMISSION STANDARD IN AUSTRIA
(1984)

	mg/Nm ³
particulate matter	50
hydrochloric acid (Cl ⁻)	100
hydrofluoric acid (F ⁻)	5
sulfur dioxide (SO ₂)	300
total lead and zinc (Pb, Zn)	5
arsenic (As)	1
chromium (Cr)	1
cadmium (Cd)	0,1
mercury (Hg)	0,1

RESULTS

At present there are several studies ongoing to implement the new laws and regulations in Austria. At the same time new disposal facilities are in the design and construction phase. Two of the most advanced plants will be described in details below.

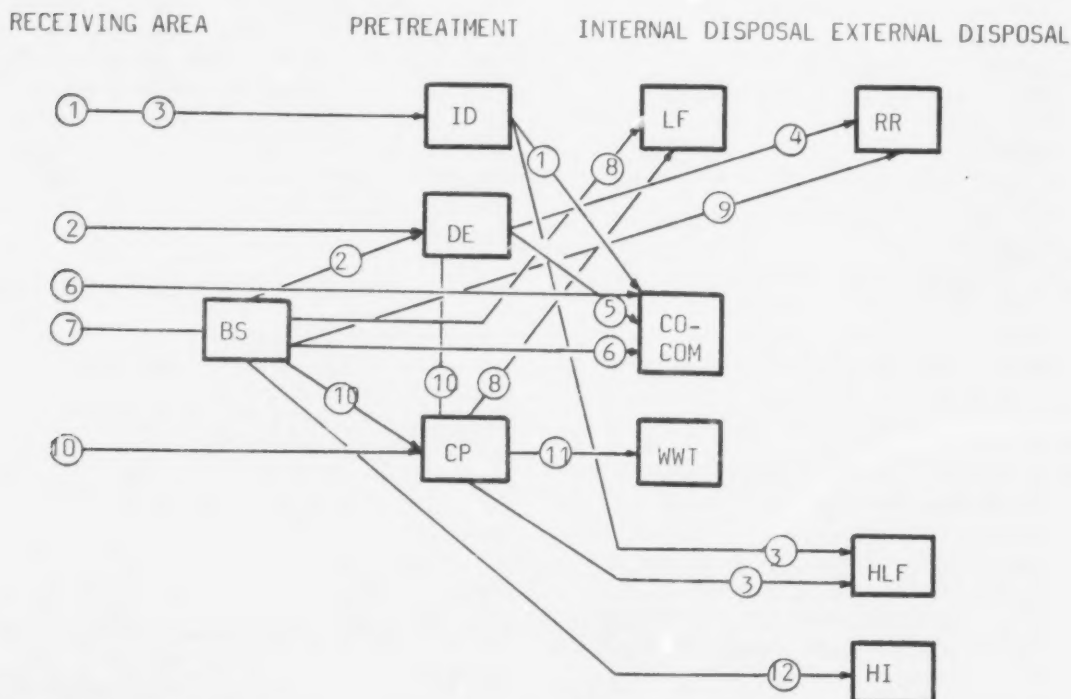
Hazardous waste collecting and transfer station in Siggerwiesen/Salzburg.

The Province of Salzburg with a permanent population of 442 000 without tourists is the only one in Austria

which has a central hazardous and toxic waste collecting and transfer station. The facility is located in the municipality of Bergheim in Siggerwiesen north of the City of Salzburg (Figure 1).

Originally the hazardous waste station was designed as a waste oil and emulsion separation plant and was put in operation in 1978. The station is connected with a

Figure 1. SCHEME OF THE HAZARDOUS WASTE COLLECTING AND TRANSFER STATION IN SIGGERWIESEN/SALZBURG.



Legend to figure 1.:

- | | |
|---|--|
| 1 contaminated solids (oil polluted soil, used oil filters, etc.) | recycling processes (solvents, batteries, etc.) |
| 2 mixture of oil, water and solids (oil emulsions, waste oil, etc.) | 10 inorganic contaminated industrial waste water (galvanic wastes, acids, caustic solutions, etc.) |
| 3 inorganic contaminated sludges and solids | 11 decontaminated filtrate of the CP-plant |
| 4 treated waste oil | 12 hazardous waste qualified for incineration (waste paints, solvents, hospital waste, PCB, etc.) |
| 5 water and sludge with few oil residues | BS barrel storage |
| 6 biologically decomposable solid or liquid hazardous wastes | ID solids intermediate deposit |
| 7 contained hazardous waste | CP chemical-physical treatment plant |
| 8 inert depositable hazardous waste | CO-COM co-composting plant for municipal solid waste and sludge |
| 9 hazardous waste suitable for | |

Continue legend to figure 1.:

LF landfill

WWT waste water treatment plant

HLF hazardous waste landfill

HI hazardous waste incineration

RR resource recovery systems.

- waste water treatment plant for an area of 350 000 population equivalent, 21 000 kg BOD₅/d, 2 000 l/s peak flow;
- co-composting plant for 400 t/d municipal solid waste and 120 t/d sewage sludge;
- paper and plastic separation for 20 to 100 t/d;
- storage and landfill with the capacity of 500 000 m³;
- emergency pond with 500 m³.

The capacity of the original waste oil separation plant amounted to 100 m³/d.

In 1984 there were 10 182 tons of hazardous waste trucked by hauling companies or private vehicles to Siggerwiesen, whereas the largest quantity in the range of 6 100 tons consisted of sludges which were composted. The decision whether an incoming material can be composted is taken by the company chemist. There is a well equipped laboratory existing with 4 chemists checking the the toxic and hazardous substances of the waste.

From the receiving area the waste is directed to the pretreatment or directly to the internal disposal. Pretreatment can be executed in the waste oil and emulsion separation plant, CP-plant (decontamination, detoxification, dewatering, etc.), intermediate deposit or barrel storage. The internal disposal is possible in the co-composting plant, central waste water treatment plant or the landfill. The Siggerwiesen landfill is located within the same property (total

acreage 80 hectares) and has the capacity of 500 000 m³. The landfill is permitted for disposal of bulky waste, white goods, screening residues, industrial waste and non toxic hazardous waste.

All materials that cannot be treated or disposed internally are trucked to external treatment plants. In Austria or abroad several recycling plants are available for processing heavy metals, solvents, batteries, tyres, etc. In case of material with high calorific value, there is the EBS-hazardous waste incineration plant in Vienna. Hazardous waste landfills are not in existence as yet in Austria and the remaining residues are usually trucked to Germany.

Hazardous waste treatment plant EBS-Entsorgungsbetriebe Simmering

In 1976 the EBS corporation was formed by the City of Vienna through the Vienna Holding and Messrs. BIA, whereby both partners are sharing approximately 50 %. In the fall 1976 the city council passed a 20-year contract with the EBS.

As a result of heavy negotiations and alterations the plant was redesigned in 1978 within a very short time period. The capacity was agreed upon 1.4 million m³ raw sludge with 5.5% dry substance and 160 000 tons hazardous waste annually. The modification was stipulated in a further contract with the City of Vienna covering the disposal of 60 000 tons annually of hazardous waste such as bar screen residues, hospital waste, industrial and commercial waste. The tipping fee was confirmed as a flat rate of \$2.8 million yearly. Together with the annual lump sum for sludge disposal the index linked fees amounted to \$4.7 million during a 20 years time period.

In addition there were existing agreements with several industrial firms as well as communities and other waste disposal facilities in Austria.

After a two years construction period the plant was started up on June 30, 1980. The total investment and start up costs amounted to \$42 million. The plant has its own energy recovery system and is running independent from the electrical grid. Since December 1982 the excess heat has been sold to the central heating system of Vienna. During the first year of operation of the waste water treatment plant and the incineration plant, problems occurred due to the bad sludge condition and also political considerations that resulted in a joint operation management.

Table 2. EBS DESIGN PARAMETER

Hazardous waste:		
total quantity,	t/a	160 000
burnable,	t/a	100 000
CP-treated,	t/a	60 000
Sludge:		
quantity raw sludge,	m ³ /a	1400 000
dry substance,	%	4-7
calorific value of the dry substance,	kJ/kg	16 300
Emissions:		
particulate matter,	mg/m ³	100
grey value,	-	1
hydrogen chlorine,	mg/m ³	100
carbon monoxide,	mg/m ³	500
hydrogen fluoride,	mg/m ³	5
total sulfur dioxide,	kg/h	325
organic carbon,	mg/m ³	50

Process description

Sludge:

The capacity of the EBS plant amounts to a daily maximum of 3 800 m³ raw primary and secondary sludge with 5.5% dry substance. The sludge is

pumped from the thickeners of the central waste water treatment plant to the sludge holding tanks where a circular sludge pumping main is installed. Dosing pumps are feeding the centrifuges and at the same time a polymer solution is added into the front end of the centrifuges. The filtrate water flows back into the waste water treatment plant. One third of the dewatered sludge is dried in two sludge dryers and afterwards it is mixed with the remaining dewatered sludge in order to get 35% dry substance in the mixture. The mixed sludge is lead into two fluidized bed incinerators. The combustion occurs at temperatures of about 850 °C.

Hazardous waste:

The hazardous and toxic waste can be delivered by rail or road. There are possibilities for delivery by barge also, because the plant is located at the Danube Canal and this option will be considered in the future. In emergency cases helicopter transportation is practicable. The hazardous waste is contained in tanks, barrels or special vessels and boxes. It is accepted in different receiving areas such as a tank farm, barrel storage, CP-plant, deposit basin, shredder pit or solid waste pit.

After separation of water in the CP-plant or in vertical tanks the liquids are pumped to burners and lances at the front end of the rotary kilns or directly into the afterburner chambers. According to the origin and composition of solid hazardous waste it is dumped into the waste pit of the shredder and the sized material is conveyed to the large pit of the rotary kilns. Hospital waste and other identified solid materials are dumped directly into the large pit. A semi automatic grab crane is feeding the charging devices of the

incinerators. The calorific capacity of each kiln amounts to 102 GJ per hour and the combustion temperature ranges between 1 000 and 1 350°C in order to destroy chlorinated hydrocarbons.

Flue gas treatment:

The flue gas of the combustion chambers of the sludge dryers is cleaned in cyclones and tube filters. In addition one dryer is equipped with a venturi scrubber.

The flue gases of the four combustion units pass boilers and produce steam with 350°C and 53 bar pressure. After cooling down to 240°C the particulate matter is removed in double field electrostatic precipitators. In addition the two rotary kilns are equipped with dry scrubbers using lime dust. ID fans are blowing the clean gases into three stacks, each of them 50m high. The emission rates and concentrations are limited by the air pollution authority, which is also controlling them.

Energy recovery:

The four boilers are producing a maximum of 90 tons per hour steam, which is utilized in two units of counter pressure turbines and generators with a capacity of 4.6 MW each. Approximately 40% of the produced electricity is used in the plant itself. The surplus in heat and electricity is sold to the central heating system of Vienna and to the central waste water treatment plant.

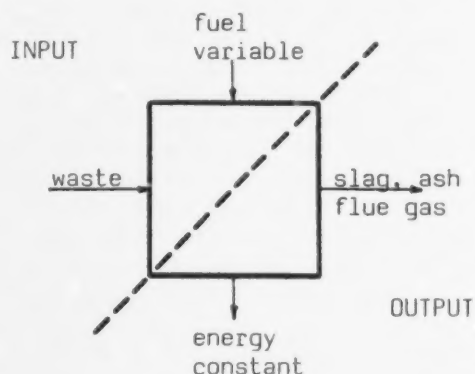
Operating experience

During the first year of operation the EBS management was faced with a number of unexpected difficulties. The new Federal Waste Oil Act came in force on January 1, 1980. This

act classifies waste oil as a marketable product without setting standards for contamination limits. Therefore the predicted quantity of waste oil decreased rapidly and was no longer available. In order to keep a proper energy balance fuel had to be added.

The design of the EBS facilities and the economics are based on a balanced energy input and output. In case of a decrease in the calorific value of hazardous waste, fuel has to keep sufficient burning conditions. The excess energy is always constant, but the quantity of residues such as slag, ash, flue gas varies in accordance with the material that has been burned. The following diagram shall illustrate the correlation.

Figure 2. CORRELATION BETWEEN INPUT AND OUTPUT IN A WASTE TO ENERGY SYSTEM



In the first year of operation 1980/1981 the input quantity of raw sludge amounted to 797 000 m³ with 4.8% dry substance and after dewatering the fluidized bed incinerators were fed with 146 000 tons. In the two rotary kilns had been burned 39 000 tons hazardous waste. In order to maintain the proper energy balance oil fuel in the range of 19 000 tons had been added. In 1983 the following hazar-

dous waste quantities were burned.

Table 3. HAZARDOUS WASTE QUANTITIES
(1983)

	t/a
organic waste solid and pasty	6 600
organic waste liquid solvents	17 800
halogenated, sulfuric wastes, poisons, etc.	1 100
oilcontaminated soil	3 600
inorganic waste	1 000
screening residues	8 600
barrels	900
hospital waste	4 500
commercial and industrial waste	13 500
waste oil	14 400
summary	73 000

In addition to the mentioned 73 000 tons of hazardous waste (including 14 400 t waste oil as fuel) the EBS took over 830 000 m³ sludge with 5.4% dry substance. The energy output amounted to 270 000 MWh steam sold to the central heating system and from a total of 32 000 MWhour produced electricity 11 500 MWhour were used in the central waste water treatment plant. The quantity of ash and slag amounted to 31 700 tons. (Figure 3.)

Future aspects

Due to the increased air pollution protection requirements additional air cleaning devices will be installed in the near future. The new emission standards are especially focused on heavy metals in the flue gas. Each incinerator will be equipped with multi stage wet air scrubbers and a central waste water neutralisation and decontamination plant will be implemented.

The existing CP-plant will be split-up into two plants. In the near future inorganic hazardous and toxic waste will be treated in a separate new plant. This plant will take over caustic solutions, extraction liquors, acids, chromates, nitrites, sludges, etc. to a maximum of 30 000 tons per year. The existing CP-plant for organic hazardous waste will be refurbished and extended to a maximum capacity of 50 000 tons annually.

The CP-plants as well as the incinerators are generating residues such as dewatered sludge, slag and ash. Because of the toxicity of these materials, they have to be deposited in an absolutely safe and controlled way together with other hazardous and toxic solids collected by EBS. Therefore studies are ongoing with a multi barriere cassette-landfill. The waste will be separately deposited in cassettes according to its origin and composition. The cassettes are completely ceiled and equipped with emission controlled systems.

ACKNOWLEDGEMENTS

The information in this report has resulted from many studies, designs and consulting services as well as practical experiences of the authors. Dr. Willibald Lutz is a member of the commission of the Austrian Environmental Fund and a consultant to the Minister of Health and Environment. Friedrich Hübl is the founder and former shareholder of the EBS-plant in Vienna. Now he is the head of a waste management company in Austria.

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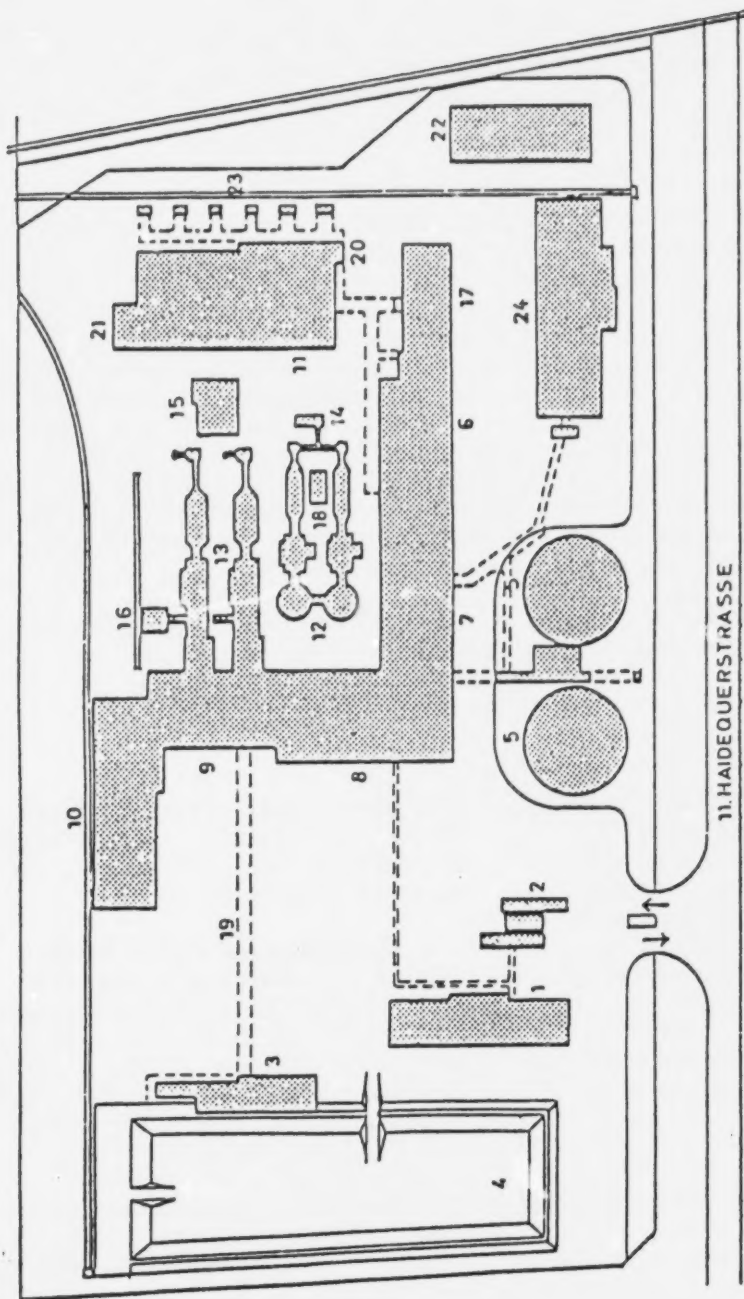


Figure 3. LAY OUT PLAN OF EBS-VIENNA (1984)

- | | | |
|--------------------------------|---------------------------|--------------------------|
| 1 administration building, lab | 9 waste bin | 17 cooling plant |
| 2 weighbridges | 10 barrel handling area | 18 measuring center |
| 3 shredder | 11 tank farm | 19 collector tunnel |
| 4 deposit basin | 12 fluidized bed reactors | 20 pumping station |
| 5 sludge holding tanks | 13 rotary kilns | 21 fire fighting station |
| 6 energy supply area | 14 starting steam boiler | 22 workshop |
| 7 control center | 15 lime dosing, ash silo | 23 filling station |
| 8 sludge treatment area | 16 slag removal | 24 CP-plant |

POLICY TRENDS IN HAZARDOUS WASTE MANAGEMENT IN ASIA AND THE PACIFIC REGION

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ABSTRACT

In the Asia and the Pacific region, there is increasing awareness of the need for sound management of hazardous wastes. With over half the world's population, accelerating development programmes and rapid urbanization trends, the impacts on environment and human health can be very serious, if appropriate control and management measures are not implemented. In the formulation and implementation of policies for managing hazardous wastes the trend is to overcome a number of major constraints. These include lack of:- information on the sources, quantity and types of wastes generated; trained manpower and financial resources; effective co-ordination amongst the ministries that are involved; specific laws and legislations; rigorous enforcement and appropriate incentives; specialized technical know-how and education and training schemes focussed particularly on improving the management of hazardous wastes.

The paper discusses the issues emanating from generation to final treatment and disposal from institutional as well as technical considerations.

INTRODUCTION AND PURPOSE

The Asia and the Pacific region is vast and according to the UN designation, it consists at present of 39 member countries. In mid 1983, the region had a population of approximately 2.6 billion with average annual growth rates varying between 1.28 and 2.16 per cent for East and South Asian countries respectively. The region's population is expected to increase to about 3.4 billion by the end of this century.

Countries in the region provide extreme contrasts in almost all aspects. The most and least populated countries; highly industrialized and least developed; land locked and island countries; the highest moun-

tain and deepest ocean; tropical forests and deserts; largest areas of mangroves and corals, etc. are found in the region.

A common prediction is that most if not nearly all countries will experience significant growth rates, with the Association of South East Asian Nations (ASEAN) countries in conjunction with the other Pacific Basin countries and the Republic of Korea, providing the lead.

Manufacturing, raw material-processing, agriculture and infrastructure developments are seen to be the major sectors that will be receiving major emphasis to promote growth.

It is clear, therefore, that irrespective of whatever development patterns and economic systems the countries in the region are embarking upon, the problems associated with hazardous wastes are already significant in those that are industrialized and will soon be for those that are fast developing.

Although awareness of and concern for the impacts of hazardous wastes are increasing, the level varies greatly between countries. However, a growing number of countries are in the process of formulating policies and strategies to manage hazardous wastes.

The purpose of this paper is an attempt to provide an overview of the major policy elements which are being considered as well as the problems encountered, from the generation to final disposal/destruction of hazardous wastes -- the "cradle-to-grave" approach. Both the technical and institutional aspects are discussed.

PROBLEM AREAS

The major problem areas which need to be overcome in order to formulate and implement effective and pragmatic hazardous waste management policies are seen to be the lack of:- information; resource; co-ordination; laws and legislations; enforcement; incentives; technical know-how, and education and training.

Although these problem areas are no different from those experienced in the industrialized countries, the situation in the developing countries is accentuated and compounded because of weak institutional mechanisms for dealing with general pollution and environmental

issues. These problems are briefly discussed in the following sections.

Information

There is a lack of information on the sources of hazardous waste, the quantity and types that are generated, the disposal methods used and inventory of storage and/or disposal sites. Without such information and data it is very difficult for national authorities to develop rational policies and implement pragmatic management procedures.

Thailand, Malaysia and India are some of the countries that are collating and compiling waste generation data.

While definitive data are not available on the quantities of hazardous waste generated, the growth in manufacturing of selected sectors of industry in India will provide an indication of the probable increase in waste streams.

TABLE 1. GROWTH PATTERN OF SELECTED INDUSTRIES IN INDIA (1)

	Production x10 ³ tonnes	
	1970	1980
Pesticides	3	41
Dyes & Pigments	14	31
Organic chemicals	17	24
Caustic Soda	304	457
Non-Ferrous (Cu, Pb, Zn)	35	83

In Thailand, a 1979-1980 study by the Office of the National Environment Board showed that wastewater from

over 50 percent of industries contained at least one kind of heavy metal with concentrations higher than the limits set by the standard. According to another survey in 1981, nearly 600 industries, the majority of which are located in and around the capital of Bangkok, dispose of wastes containing mercury, nickel, chromium and cadmium.

Acquisition of information and data can be an expensive and time consuming undertaking. Before such an effort is made, a careful review of whether such information and data already exist in the various ministries, research establishments, academic institutions and industrial enterprises is undertaken. Collation of existing information and data would preclude the need for unnecessary expenditures. If information and data need to be acquired, then the specific uses are identified first, so that only relevant information and data would be compiled and presented in the appropriate format for the intended use.

Resources

Most if not all countries lack adequate resources to manage and dispose of hazardous wastes. This constraint is much more acute in the developing countries. There is already a shortage, and in many countries a critical shortage, of trained and experienced manpower, facilities as well as financial resources.

During the past decade the number of environmental issues confronting governments and industry have increased significantly. These have evolved from site specific and end-of-pipe pollution control to global common issues such as ozone layer depletion and carbon dioxide

build-up, transboundary problems of acid rain, as well as loss of wildlife and genetic species.

The awareness of hazardous waste problems is relatively recent. Governments are finding it increasingly difficult to allocate budgets, since there are other major competing needs for financial resources, including budgets for controlling and abating conventional pollutants. There is a hesitancy to divert and/or increase manpower and resources from on-going environmental programmes. Hence, the availability of reliable information and data is important, in order for governments to assign priorities and allocate appropriate resources.

A strategy which a number of countries are considering is a variant of the polluters pay principle, with the government providing the supervision and operating the facilities for a fee.

Co-ordination

Most countries in the region continue to regard hazardous waste as primarily solid waste and are "managing" it under existing institutional mechanisms. In most cases this is done under municipal waste collection and disposal procedures and methods. Industrial wastes are left to the individual industries to dispose of and as in the case in Thailand and Indonesia, for the Ministry of Industry to supervise and enforce any existing regulations. Hospital wastes are normally the responsibilities of hospitals and the Ministry of Health. Similarly, agrochemicals and minetailing wastes are the responsibilities of the Ministries of Agriculture and Mines respectively.

During the past five to ten

years most countries in the region have established Ministries and/or Departments of the Environment. These new institutions are now beginning to recommend overall policy guidance, improve co-ordination amongst the various ministries and follow-up on enforcement measures.

Their role in increasing awareness of the problems of hazardous wastes, using such well reported cases as the Love Canal and Times Beach in the U.S. and the Lekkerkerk in the Netherlands, is beginning to support the need for better co-ordination in the formulation and implementation of policies for managing hazardous wastes.

Laws and Legislations

In the region, laws and legislations for the control of hazardous waste are generally embodied in a variety of other legislations that deal with environmental and health protection, resource recovery, factory safety, etc. There are at present no specific legislative acts specifically promulgated for hazardous wastes.

In Japan for example, the Basic Law for Environmental Pollution Control enacted in August 1967 provided the framework for controlling hazardous wastes. More significantly the series of prohibitions on the production, use and importation of PCB between February 1971 and September 1972 (2) underscored the priority placed by the government on the issue of controlling hazardous waste.

In a large number of countries, the definition/criteria for hazardous wastes are still being discussed and debated.

While the characteristics most commonly used to designate hazardous waste:- toxicity, reactivity, corrosivity and flammability are used, for example in Australia (3), there is as yet no general agreement. The system of an inclusive and/or exclusive lists (4) for classifying hazardous wastes is also being contemplated by a number of countries.

A trend in an increasing number of countries is to review existing legislations and assess whether these are adequate for the control and management of hazardous wastes as well as determine whether there are any gaps which need to be specifically filled.

One particular area which needs special attention is in the transportation of hazardous wastes from the generating source to either interim storage and/or final disposal sites. Since transportation by road, rail, waterways or sea is the responsibility of many different ministries, including the Police Department, the trend is to ensure that any licencing and manifest systems introduced are effectively coordinated and enforcement responsibilities clearly delegated and accountable.

In this regard, interministerial committees are being established to enhance cooperation and coordination.

Enforcement and Incentives

The infringement of laws normally carry a paltry penalty. Often it is less expensive and more expedient to continue paying the fine than to incur proper treatment and disposal costs. In Japan for example, in 1979, 4,778 of the 5,855 arrests for pollution offences were connected with wastes.

While the penalty for violating hazardous waste legislations needs to be increased, because of the severity of the effects on human health, there should also be at the same time incentives for the waste generators to improve and/or change processes and operations that do not result in hazardous wastes. Instruments such as tax rebates, subsidies, low interest loans could be considered by governments to encourage such changes.

Technical Know-How

Reduction at Source

There is growing recognition, based on the experience of the industrialized countries, that preventive policies are in the long run more cost effective. While there is awareness of the availability of technologies which do not form hazardous wastes, for example, the use of the membrane process instead of mercury cells for the manufacture of caustic soda, the substitution of PCB's, and the recycling and recovery of toxic components of residues, there is still general reluctance to change over from conventional processes. This is because of costs, and only greenfield installations can consider incorporating such new processes, as well as the perceived risks involved with the performance of such processes.

Fiscal instruments described earlier could be used by governments to promote the use of less hazardous processes. Similarly, demonstration projects could also be constructed to show the efficacy of recovery and recycling.

Storage and Transportation

The majority of the industries

generating hazardous wastes in the region are of small scale. Similarly, those emanating from individual non-industrial origins, such as from laboratories and pesticides use are also small volume at source. As the wastes have no economic value, there is a tendency to store them in used containers which will be discarded. The conditions of these containers are such that they leak readily, discharging their contents. This was a case in Thailand where a recent leakage of waste ethyl acrylate from old container drums hospitalized about 300 workers.

There is scope for the design of reception centers capable of accepting the safe storage of small volumes of hazardous wastes.

While there are the Recommendations of the United Nations Committee of Experts on the Transport of Dangerous Goods, which began its work in 1953, very few countries in the Asia and Pacific region have used these recommendations as a framework for promulgating national regulations.

With increasing awareness and concern by governments, industry and the general public on environmental issues, the trend will be to develop a system of technical and legislative measures that will be both efficient and reassuring, securing the safety of all without excessively penalizing the economies of production or being an obstacle to trade. The developing countries in the region are learning from the experience of the industrialized countries and are keen to avoid the mistakes that have been made.

Treatment and Disposal

Land filling:- At first this would seem to be an option which could

be widely used in countries in the Asia and Pacific region. However, there are now serious considerations, particularly in the developing countries because of the difficulties in securing the land filled site. Scavenging of waste dumps is a widely practised occupation in most developing countries. Another growing concern is with the potential contamination of ground water supplies.

The resistance of the people to the planned disposal of thorium hydroxide in concrete dump ditches spread over a 5-hectare site in Malaysia, is an example of the concern that is emerging with land filling methods.

Incineration

For wastes which have sufficient calorific value, such as spent oils and solvents, and concentrated organic solutions final disposal by incineration is considered as a viable method. However, at present, when this disposal method is used, it is not used effectively. Combustion is inefficient and often incomplete. The generation of secondary air pollutants is generally not considered, as should be the case, for example of chlorinated hydrocarbons.

Chemical Treatment

Processes such as neutralization, oxidation, reduction and precipitation are used, even in small scale industries such as metal plating and chrome leather tanning.

There is, however, significant scope for optimization of these treatment processes to improve efficiency. An important incentive to increase the use of chemical treatment options is the added

benefit of the potential for material recovery and recycling.

Ocean Dumping

With the exception of Japan, there is very little published information on whether this method is used and also whether the London Dumping Convention is followed. In Japan, ocean dumping is closely regulated and discharge methods are classified as either concentration-type or dispersion-type. Discharge areas are designated for industrial hazardous wastes; wastes which are not returned to the ocean, and wastes returned to the ocean (5).

In many countries, it is very likely that installations situated near coastal areas are discharging their untreated wastes directly into the sea. Heavy metal contents in fish and other marine organisms are evidence of such clandestine practices. Although most countries have laws prohibiting such practices, enforcement is very difficult.

Treatment and Disposal Options

Most if not all the developing countries in the Asia and Pacific region lack sufficient studies and experience to be able to assess and determine which option or combination of options will be most appropriate to meet national needs. Presently policies are formulated primarily based on the reported information and/or experience of the developed countries.

Often technologies are transferred with very little adaptation to local conditions.

Education and Training

The importance of education and

training in environmental management, including hazardous wastes is recognized. Education and training are accorded top priority by all Ministries and Departments of Environment in the region.

There is a trend for countries to consider developing and implementing comprehensive programmes which encompass both formal and non-formal strategies. Audiences, ranging from decision-makers to youth and the general public are targeted and print, radio and television media are used to increase awareness.

Australia, for example, focussed on hazardous wastes in its 1984 World Environment Day publicity and information programme.

Universities in the region are also beginning to offer credit courses on hazardous waste management in their education programme.

RESULTS

The overview indicates that the industrialized countries -- Australia, Japan and New Zealand -- in the region are already implementing hazardous waste management schemes, similar in scope and content to those of other industrialized countries in Europe and North America.

The countries that are fast industrializing, for example, Singapore, Republic of Korea, India, Thailand, Malaysia, Indonesia and Philippines are increasingly recognizing that there could already be some hazardous waste problems, but are uncertain with regard to their seriousness, because of lack of information. It is clear, however, that there is no doubt amongst these countries on the potential impacts of

hazardous wastes on human health and the ecosystem, if proper management and control measures are not instituted now. Without exception these countries are endeavouring to learn from the experience of all the industrialized countries. The advice and information received are carefully assessed and synthesized and are beginning to be forged and adapted for national use.

For countries that are still primarily agriculture based, there is still a need to be concerned with the disposal of used products such as lead batteries, and containers for pesticides. It is not an uncommon sight to see such containers used as water cans, with minimal rinsing and/or decontamination.

Undoubtedly, hazardous wastes need to be managed within the context of an integrated environmental management policy and strategy.

The countries in the region recognize the need for such an approach and the policy trends, institutionally and technically, are beginning to underscore this.

ACKNOWLEDGEMENT

I am grateful to my associates in the United Nations Environment Programme for the useful discussions on managing hazardous wastes and to colleagues in the various Ministries and Departments of Environment in the Asia and the Pacific region for sharing their concerns and thinking on this subject. However, I take responsibility for any erroneous interpretation and the views stated are my own and do not necessarily represent the policies of the United Nations Environment Programme.

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THE DETERMINATION OF FIXATION TREATMENT METHOD
LIMITS FOR HAZARDOUS LIQUIDS AND INDUSTRIAL SLUDGES
FROM DISPARATE SOURCES

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ABSTRACT

The disposal of industrial waste sludges has been an operating problem to industry and landfill operators for many years. In past years, designers failed to complete their responsibility by adequately addressing the disposal requirements of the sludges produced by industrial waste treatment plants. Most often, the waste treatment plant operator was presented with a sophisticated treatment facility which produced a high quality effluent but also produced large volumes of raw, gelatinous sludges with no dewatering equipment and inadequate means for disposal. Disposal of these sludges has been a costly operating problem to industry.

As landfill designs and operations became regulated in the United States during the 1970's, the disposal costs for industrial sludges increased significantly. Eventually, liquid sludges could no longer be accepted at landfill disposal sites. This renewed a market for improved sludge dewatering facilities. It also created a new market for solidification and stabilization processes and for chemical fixation of hazardous liquids and sludges.

Many of these dewatering and sludge solidification/fixation processes were evaluated for use at a new commercial hazardous waste disposal plant. This disposal firm processes 100,000 gallons per day (gpd) of various hazardous inorganic liquids and industrial sludges, mostly consisting of acids, alkalis, and plating wastes.

After the fixation process was selected, based upon general application tests, a battery of tests was conducted to determine the limit to which the fixation process would treat effectively various hazardous inorganic liquids and industrial sludges. These tests were then used to limit the type of acceptable incoming wastes, to develop plant operating guidelines, and to form the basis of information to obtain a temporary delisting from the State and the EPA, for the wastes treated at the facility.

The fixation process selected employs lime, cement, and bentonite addition to the wastes. The lime is used to optimize pH for heavy metal precipitation, the cement solidifies the treated wastes within approximately 48 hours, and the bentonite acts to bind the metals by ion exchange as well as reducing the permeability of the fixed wastes.

The test methods used in the determination of the leaching characteristics, the limits of treatability, the nonapplicability to some wastes, and the pretreatment standards for the fixation used at the waste treatment facility are reviewed in this paper.

INTRODUCTION AND PURPOSE

The use of fixation treatment methods to render hazardous liquid wastes to a nonhazardous solid is hampered, to a great degree, by the unknown treatment limitations of the specific process. This paper describes the tests and rationale that were used to delineate the treatment limitations of a specific fixation treatment process. The tests described herein were conducted in conjunction with a successful delisting petition.

The purpose of the tests was to define the level of contamination in raw liquid wastes that would cause the fixated material to fail the EP toxicity criteria, to interfere with solidification process, and to address the long-term stability of the fixed material under rigorous and natural weathering conditions.

APPROACH

In order to define the specific treatability limitations of the fixation treatment system, a battery of spike tests were set up.

It was planned that these tests would identify the concentrations of each metal that would overload the solidification/fixation process and cause the treated wastes to fail the EP toxicity criteria, thus establishing a maximum concentration level that could be processed by the treatment facility. Raw liquid hazardous wastes from a variety of industrial sources were collected and analyzed for heavy metals (barium, cadmium, chromium, lead, mercury, nickel, silver, arsenic,

and selenium), cyanide, and phenol content. The raw liquid hazardous waste sample was then divided into three samples, A, B, and C. Sample A was spiked with enough barium, cadmium, chromium, lead, mercury, nickel, silver, arsenic, and selenium to produce a concentration of 0.1 percent (about 1,000 mg/l) for each metal. Samples B and C were similarly spiked to produce individual metals concentrations of 0.5 percent and 1.0 percent, respectively. Using this metals spiking procedure produced a total metals concentration of about 0.9 percent in A, 4.5 percent in B, and 9.0 percent in C. (Chromium was added in the hexavalent form, and analysis was conducted for total chromium. All metals were spiked as the metal compounds commonly used for internal standards in standard additions spikes for chemical analysis.)

The spiked raw waste samples were analyzed to determine the actual metals concentration and then were fixed. The fixed samples were EP leached after 24 hours of curing time and leachate was analyzed for the nine heavy metals. Another portion of the raw liquid hazardous waste was divided into three portions and spiked with enough cyanide and phenol to yield the following raw waste concentrations:

Sample Group	Cyanide	Phenol
A	17 mg/l	0.35 mg/l
B	4.5 mg/l	1.3 mg/l
C	2.9 mg/l	1.6 mg/l

These spiked raw waste samples were then fixed and leached after 24 hours of curing. The leachate was immediately analyzed for cyanide and phenol.

In order to delineate the leachate quality of the fixed materials over extended rigorous leaching conditions, a battery of tests was set up. These tests used fixed materials collected from an operational, full scale, fixation treatment plant. The fixed materials were allowed to cure for three days. The fixed material was ground to a 150 particle size prior to leaching. After EP leaching, the samples were subjected to the EPA Multiple Extraction Procedure. (This procedure is detailed in the Appendix.)

In order to investigate the long-term stability of the fixation process under normal weathering conditions, samples were collected from nine field test cells that had been in place for six years. The field test cells were originally constructed and used to generate data concerning weathering conditions and to support the patent applications for the fixation process. Samples were collected and composited from any discrete layers which appeared in each field test cell. The samples were then subjected to EP leaching and the leachate was analyzed for cyanide, barium, cadmium, chromium, copper, iron, lead, mercury, silver, arsenic, and selenium.

PROBLEMS ENCOUNTERED

Prior to the treatability limitation spike tests, it was observed that in spiking the raw wastes with all of the metals, the metals leached or reacted to the EP leaching in a synergistic manner. That is to say that two metals in sufficient quantities may complex with each other to form a highly leachable or

soluble complex, or a nonleaching or insoluble complex. It was assumed that these interferences could be identified by comparing the constituent analyses of the spiked raw wastes and fixed wastes and in a graphic analysis of total raw waste content versus leachate content. These types of effects were noted by some variations in apparent barium fixed material content in each of the three trials (approximately 0.1, 0.5, and 1.0 percent). Arsenic and selenium variation from spiked raw waste acid to spiked fixed waste occurred in only the 0.5 percent addition trial. Each of these apparent synergistic effects formed insoluble complexes.

Another problem encountered was that the multiple leach tests may not be representative for phenol because of possible biological digestion of the phenol. This did not appear to be a problem once the data were examined for a mass balance of phenol content in the fixed material to the phenol content in the multiple leaches.

RESULTS

Inorganic Solidification/Fixation Treatability Limits

After the analysis was completed on the inorganic spike tests and graphically plotted to compare liquid raw waste metal content to fixed material EP leachate metal content, it was apparent that the nine metals could be put into three groups. The first group were those with metals with leachate concentrations not significantly elevated by the metals spiked to the raw wastes. These metals included barium, lead, silver, and arsenic. (The data are presented in Table 1.) The treatability limit of these metals was not approached by the metal concentrations spiked to the raw wastes and remained below 1 mg/l.

The second group of metals were those with leachate concentrations

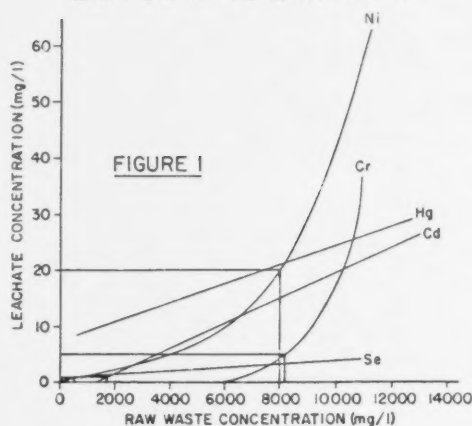
linearly elevated by the metals spiked to the raw wastes. These metals include mercury, cadmium, and selenium (see Figure 1). From Figure 1 and Table 1 it can be observed that mercury, cadmium, and selenium leached from each of the three spiked samples above the EP toxicity limit. However, each of the three metals leached in a very nearly linear proportion. The cadmium and selenium leaching curves intersect the level of EP toxicity allowing the leaching limits to be estimated for each of the metals. The mercury leaching curve did not intersect the EP toxicity limit of mercury indicating that the curve probably has an inflection point at the very low end of the curve. This level of raw waste mercury concentration versus leachate mercury concentration should be investigated further in order to locate the fixation limit for mercury.

TABLE 1
(mg/l)
ANALYSIS OF RAW WASTE AND EP LEACHATE
AFTER CHEMICAL FIXATION/SOLIDIFICATION
SPIKED SAMPLE CONCENTRATIONS

	0.15		0.55		1.05	
	Raw Waste Total Analysis	EP LIMIT	Raw Waste Total Analysis	EP LIMIT	Raw Waste Total Analysis	EP LIMIT
Ni	15	0.5	2000	0.7	6000	< 0.1
Cd	2000	0.3	10000	0.35	10000	0.3
Cr	1710	0.05	5000	0.05	10000	0.3
Pb	1170	0.05	2500	0.05	10000	0.3
Hg	1000	0.4	100	0.4	11000	0.4
Se	1300	1.05	1000	0.4	11000	0.4
Ag	200	0.05	1700	0.05	2000	0.05
As	1100	0.05	1000	0.05	12000	0.05
Sr	750	1.5	1000	2.0	7000	2.0

The third group are metals where the leachate concentrations responded nonlinearly to the metals spiked to the raw wastes. These metals include nickel and chromium. (See Figure 1 and Table 1.) Figure 1 shows that both chromium and nickel leachate concentrations increased in a nearly exponential manner once a "saturation point" was reached. However, both of these curves also intersect the EP toxic limits for the respective metals.

LEACHATE METALS CONCENTRATION VS.
RAW WASTE METALS CONCENTRATION



The overall purpose of the metals spikes was to determine the concentrations that would conservatively overload the fixed process and cause the treated wastes to fail the EP toxicity criteria. The results of these tests are given in Table 2.

Table 2
Approximate Limits of
Solidification/Fixation

Metal	Raw Waste Concentration (mg/l)
Barium	6,600
Lead	8,820
Silver	3,900
Arsenic	12,000
Cadmium	1,700
Selenium	500
Mercury	600
Nickel	8,000
Chromium	8,200

Cyanide and Phenol Solidification/ Fixation Leaching Characteristics

Early in the development of this fixation process it was suggested that organics and cyanide would not be adequately treated by the process. Exhaustive analysis of potential raw waste streams indicated that phenol and cyanide were common contaminants in the incoming raw wastes. In order to obtain some idea of the leaching of these two contaminants, spike tests and leaching tests were also conducted. Three raw waste samples were spiked with the concentrations shown in Table 3A and subsequently leached.

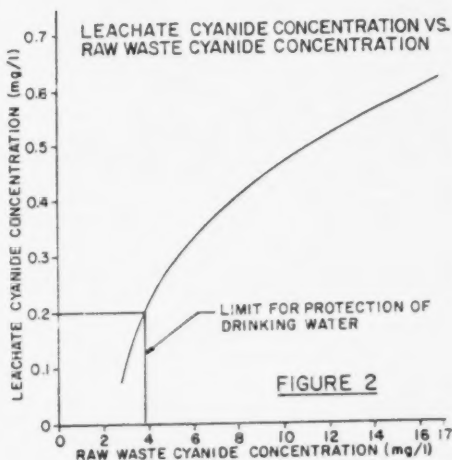
Table 3A

Spiked Raw Waste Concentrations	Leachate Concentrations
Sample A:	
Cyanide - 17	0.62
Phenol - 0.35	0.15
Sample B:	
Cyanide - 4.5	0.25
Phenol - 1.3	0.29
Sample C:	
Cyanide - 2.9	0.076
Phenol - 1.6	0.75

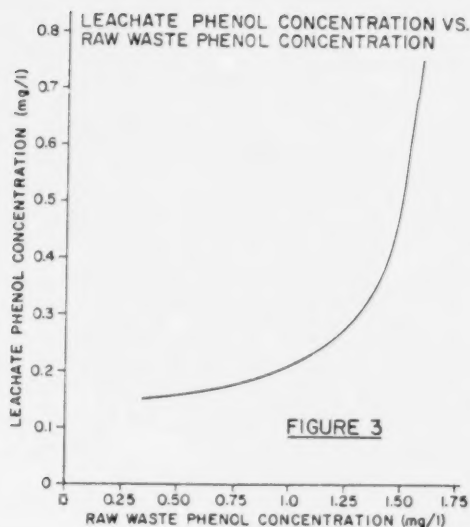
Concentrations in mg/l.

From the graph in Figure 2, it can be seen that cyanide appears to be readily leachable from the fixed raw waste. However, if the EPA Public Health Services recommended limit for the protection of drinking water (200 g/l) is applied to these results, an apparent limit of 3.8 mg/l of cyanide can be effectively treated by the fixation process. Limits for cyanide in terms of EP

toxicity have been established but in terms of its possible hazardous nature due to reactivity, EPA advises that a solid should contain no more than 20 mg/kg of cyanide. The highest concentration of cyanide added to the raw waste was 17 mg/l which, when fixed, leached only 0.62 mg/l.



From the graph in Figure 3, it can be seen that phenol appears to leach in an exponential manner when compared to the amount of phenol spiked to the raw acid. However, none of the leachate phenol concentrations exceeded the EPA Public Health Services recommended limit for the protection of drinking water of 3.5 mg/l. From the apparent slope of the leaching curve, it is hypothesized that this limit would be reached rather quickly at higher phenol concentrations



Multiple Extraction Data

The previously discussed spike tests outline the effect that raw waste contaminant content has on leachate of the fixed material, but in only a single leaching step. This leads to the question, "What effect will prolonged exposure of the fixed material to an aggressive leaching media have over a longer period of time?" In an attempt to answer this question, a set of multiple extractions were conducted as outlined in the Approach section above.

The data from these inorganic tests were analyzed by graphing the individual EP toxic metals leaching over the multiple extractions and graphing the total EP toxic metals over the multiple extractions. The data from the cyanide and phenol multiple extraction tests were analyzed by comparing the total amount of each contaminant leached during the extraction procedure to the total amount of each contaminant in the sample prior to leaching.

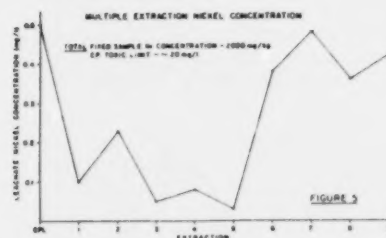
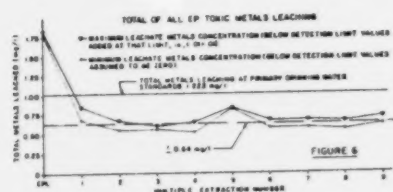
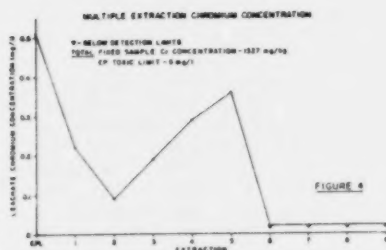
Inorganic Multiple Extraction Tests

The inorganic multiple extraction results are presented in Table 3B. The multiple extraction procedure is a very rigorous leaching procedure and is probably more severe than natural conditions. The majority of metals did not leach to any significant degree. These metals included barium, cadmium, mercury, silver, hexavalent chromium, arsenic, and selenium. Four of this group of metals (arsenic, barium, mercury, and selenium) probably did not have sufficient quantity of the metal in the treated sample to leach in any great quantity. Of the remaining metals in this group, cadmium, silver, and hexavalent chromium showed low leaching rates. The remaining three metals, chromium, lead, and nickel showed an excellent resistance to leaching after being fixed. All three of these metals were present in relatively high concentrations in the fixed sample with chromium (Figure 4) and lead leaching at below detection limit concentrations. The leachate concentration of nickel is the only leachate metal concentration in the tests that does not approach or go below detection limits in the last four extractions (Figure 5). However, at no time do any of the nickel leachate concentrations approach the EPA toxicity or drinking water guidelines of approximately 20 mg/l, with the leachate values at or below 0.5 mg/l.

To gain some idea of the overall quality of the leachate under multiple extraction, the total EP toxic metals concentration was graphed for the extraction step (Figure 6). This graph shows that the leachate metals concentration stabilizes after the second round of leaching, to a total EP toxic metals concentration of approximately 0.64 mg/l. This level of leaching is below the total metals allowed in

TABLE 3B
MULTIPLE EXTRACTION LEACHATE ANALYSIS (mg/l)

	EP	1	2	3	4	5	6	7	8	9	Total Analysis of Sample mg/kg	Limits EP Toxicity
Ba	0.6	<.2	<.1	.2	<.1	.2	.2	.1	.2	.2	<1	100
Cd	0.03	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	6.0	1.0
Hg	.0031	<.0002	<.0002	<.0002	<.0002	.0011	<.0002	.0002	.0002	.0012	<1	0.2
Ag	.04	.01	.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	5.0	5
Cr	.51	.22	.09	.19	.29	.35	<.02	<.02	<.02	<.02	1527	5
Pb	<.06	.30	.22	.13	.16	.15	<.06	<.06	<.06	<.06	165	5
Mn	.50	.10	.23	.05	.08	.03	.38	.48	.36	.42	2020	<20
Cr ¹⁶	.084	.042	<.02	<.02	<.02	.050	<.02	<.02	<.02	<.02	0.1	5
As	.006	<.001	<.001	.001	<.001	.003	<.001	.001	.002	<.001	.05	5
Se	.002	<.002	<.002	<.002	.002	<.002	.002	.003	<.002	<.002	.2	1.0
TOTALS	1.84	<0.89	<.68	<.61	<.67	<.81	<.70	<.70	<.68	<.74		



Employing the sample weight and leachate volumes, a rough mass balance of metals was calculated. The percentage of the total weight of metals leached during the complete multiple extraction procedure was 3.5 percent of the weight of metals contained in the fixed sample. If the metals had leached consistently at Primary Drinking Water Standards, more than 5 percent of the metals contained would have leached.

the Primary Drinking Water Standards which are 100 times less than the EP toxic limits.

Cyanide and Phenol Multiple Extraction Data

Cyanide and phenol were also monitored in the multiple extraction tests. The data are presented in Table 4. To analyze these data, a mass balance was performed for both contaminants. The possible mass of the contaminants leached was then compared to the total mass of contaminants contained by the fixed sample. The mass balance of both cyanide and phenol shows that the weight of contaminant in both cases is well within the maximum and minimum mass leached. This can be interpreted to mean that the fixed process provides very little treatment of these contaminants.

TABLE 4
CYANIDE AND PHENOL
MULTIPLE EXTRACTION RESULTS

Leaching Total	Leachate Concentration Phenol (mg/l)	Mass of Phenol Leaching (mg)	Leachate Concentration Cyanide (%)	Mass of Cyanide Leaching (mg)
EP Leach	0.016	0.045	0.033	0.106
Leaches 1 through 5	<.01	<.035	<.005	<.017
*Total Maximum Mass Leached	---	0.045	---	0.106
*Total Maximum Mass Leached	---	0.36	---	0.290
Fixed Material Content	---	0.058	---	0.242

*Minimum totals were generated by assuming all detection limit values to be zero, i.e., 0.01 = 0. *Maximum totals were generated by assuming all detection limit values to be at that value, i.e., 0.01 = 0.01.

EP Leachate Results from Five Year Old Field Test Cells

Composite samples from the 16 field test cells were EP leached and the leachate was analyzed for the EP toxic metals (see data Summary Table 5). Recall that these field test cells were exposed to the year round weathering conditions of western Pennsylvania for six years. These field test cells were initially used in the research and development of the fixation process. The tests were generally conducted under differing mixing, and reagent conditions that were not optimized at the time. The raw liquid wastes

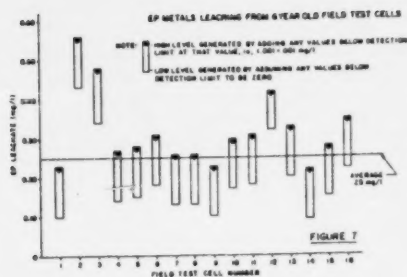
that were treated and placed in the field cells were from the same types of waste generators that provided raw wastes for the spike and multi-leach tests. The treated material produced in these early tests was not yet optimized so it can be assumed that fixed materials produced at optimum conditions would exhibit a lower leaching rate.

TABLE 5
FIELD TEST CELL EP LEACH TEST
DATA SUMMARY (mg/l)

Metal	Average	High	Low	EP Toxicity Limits
Ba	<.1	<.1	<.1	100
Cd	0.04	0.05	0.03	1
Cr	0.08	0.37	0.03	5
Pb	0.04	0.16	<.03	5
Hg (ppb)	<.5	<.5	<.5	0.2
Ag	0.03	0.05	0.03	5
As	0.006	0.016	<.001	5
Sa	0.004	0.011	<.002	1

Note: In calculating averages, any values below the detection limit were assumed to be at that limit, i.e., <.01 = .01 mg/l.

The total EP toxic metals concentration leached was plotted for each of the 16 field cell samples (see Figure 7). No values were above 5 percent of the EP toxic limit. The high and low limits for these total EP metals were then averaged to give the average total leaching EP metals of 0.25 mg/l after six years of weathering. This leaching figure is lower than the total leaching figure generated in the multiple extraction procedure, but of the same order of magnitude. It would also be expected that as available metals were leached from the fixed material that the rate of leaching would decrease. These data, therefore, compares reasonably well with the multiple leaching data.



CONCLUSIONS AND COMMENTS

This battery of fixation process evaluation tests can be characterized as a rather conservative approach, being that the tests do not actually address any of the beneficial physical properties of fixing a liquid hazardous waste.

The tests presented in this paper evaluate only a few of the beneficial mechanisms and aspects of fixing a liquid hazardous waste. The EP leachate tests, multiple extraction tests, and EP leachate tests of weathered material do not address the low permeability of the fixed material, the limitation of available surface leaching area of the fixed material, or the capacity of the fixed material to absorb and hold potential leachate. In order to understand the optimal physical effects of solidifying/fixing liquid wastes, another round of similar tests could be conducted without grinding the fixed material to pass a 150 screen and to subsequently compare such results to the results presented here.

Since the fixation system selected and employed in these tests passed the rigorous set of tests outlined by the paper with apparent ease, the positive physical properties of the process were not investigated. In another case where the fixation process did not perform so well in treating the prospective raw wastes or if additional data were needed for the design of a leachate treatment plant, the physical aspects of the fixation process should also be evaluated.

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2. 40 CFR, Part 261, Appendix III, Chemical Analysis Test Methods.
3. Multiple Extraction Procedure, Method 1320, 47 FR - 52682, November 28, 1982.
4. Test Methods For Evaluating Solid Waste, Physical/Chemical Methods, EPA Publication SW-846.
5. EPA, Methods of Chemical Analysis of Water and Wastes, EPA Method 200.0 Standard Additions.

APPENDIX

- A synthetic acid rain solution was prepared by adding a 60/40 weight percent mixture of sulfuric and nitric acid to distilled water until a pH of 3.0 (+0.2) was achieved.
- The solid phase of the fixed sample after EP leaching was weighed and placed in the EP extractor with 20 times its weight of the synthetic rain extraction fluid.

- The mixture and sample was then agitated for 24 hours at a temperature maintained between 68 and 104 F. The pH was recorded 5 to 10 minutes prior to extraction and at the end of extraction.
- The contents at the end of the 24 hour extraction period were then separated into its component liquid and solid phases as with the separation procedure in the EP leach.
- The extract was then analyzed for barium, cadmium, chromium, lead, mercury, nickel, silver, arsenic, selenium, cyanide, and phenol.
- The solid phase remaining was then subjected to reextraction in accordance with the above steps an additional eight times.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

DEVELOPMENT AND APPLICATION OF ON-SITE TREATMENT
TECHNOLOGIES FOR SLUDGE FILLED LAGOONS

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ABSTRACT

Over a period in excess of ten years, several industrial sludges were disposed of by landfilling. During the period of operation, the composition and rate of deposition of sludges varied. The resulting lagoon contains in excess of 30,000 cubic yards of sludge. Leachate from the sludges has impact on local groundwater.

Acidic, neutral and alkaline aqueous extraction of the sludges has been examined. Contact times and sludge-to-extract ratios are important parameters. Sequential extractions result in decreasing extract concentrations, implying exhaustive leaching of the lagoon is possible.

Biological treatment of naturally occurring leachate and representative extracts has been examined. Aerobic microbial treatment with unacclimated and acclimated sewage organisms results in varying degrees of organic removal. Removals of up to sixty-five percent have been achieved. A soil based microbial treatment process has been examined, also. Degradation efficiencies in excess of ninety-five percent have been demonstrated.

INTRODUCTION

Over a decade or more, several sludges were disposed of by landfilling. During this period of operation, the composition and rate of deposition of sludges varied. The resulting lagoon contains more than 30,000 cubic yards of sludge. The principal sludges in the lagoon are primary (lime neutralized) and secondary (biological) sludges from treatment of effluent from diverse chemical manufacturing operations. The sludges

range from solid to gelatinous in physical state and are layered in the lagoon. Leachate from the sludges has impact on local groundwater.

Clean-up of the lagoon is viewed as consisting of two interrelated problems. The first problem is the removal of contaminants from the lagoon, without major excavation. The second problem is treatment of the stream containing the stripped contaminants, including both organic

and inorganic species. Towards these ends, several extractants and treatment processes are being considered. Acidic, neutral and alkaline aqueous extractants have been examined for removal of organic contaminants. Aerobic and soil-based sequential aerobic/anaerobic microbial treatment processes have been examined for renovation of the resulting wastewater stream.

FORCED EXTRACTION OF SLUDGES

Extraction experiments were performed to examine applicability of forced extraction for controlled removal of organic species from the primary and secondary sludges. Studies were conducted by shaking a measured amount of sludge with a quantity of extractant. Extractants employed were acidic, neutral and alkaline aqueous solutions. The sludge-extractant mixture was shaken for the period specified for each case. The mixture was centrifuged and the supernatant solution decanted. Subsequently, the supernatant was assayed for pH, EC, TOC and TDS. Parameters evaluated included time to equilibrium, extractant pH, and extractant to sludge mass ratios.

Time to equilibrium was determined by allowing single extractions to interact from 6 to 48 hours. A minimum contact time of 24 hours was required to attain equilibrium; see Figure 1. Sequential extractions of a quantity of sludge with fresh extractant were performed. At the conclusion of each extraction step, the extraction mixture was centrifuged and the supernatant decanted. Acidic, neutral and alkaline extractants were used.

Extraction of the secondary sludge proved to be independent of extractant pH; however, extraction of

the primary sludge was dependent on pH. Typical results are presented in Figure 2. Alkaline extractant proved to be much more effective than neutral or acidic extractants. A 0.1 N solution of sodium hydroxide, at pH 13, achieved the best removal of organic matter. Satisfactory results were achieved with NaOH solutions, at pH between 11 and 12, also. Order of magnitude reductions in caustic required and extract TDS make extraction at pH between 11 and 12 desirable.

The ratio of extractant volume to sludge mass was varied, also. Ratios as small as 2 ml extractant per gram moist sludge were found to achieve high organic species removal. Extract TOCs as high as 3200 mg/l were observed. Typical results of sequential extractions are presented in Figure 3 and Table 1.

Sequential extractions of fresh quantities of sludge with the same extractant were performed, also. At the conclusion of each extraction step, the mixture was centrifuged and decanted. The supernatant was added to fresh sludge and shaken. The cycle was repeated to determine the maximum extract TOC attainable. Equilibrium was reached with five extraction steps. TOCs as high as 8900 mg/l were observed.

AEROBIC BIODEGRADATION OF LEACHATE AND SLUDGE EXTRACTS

Aerobic biodegradation of leachate and forced extracts was examined. Optimum conditions for maximum degradation of organic species were sought. Experimental parameters considered were pH, glucose as a supplementary carbon source, and initial inoculum concentration.

A stock culture of microorganisms, acclimated to a feed solution containing both glucose and leachate derived organic carbon (GOC and LOC, respectively) was used. This culture was derived from the secondary sludge of a municipal sewage treatment plant. Feed for the stock culture had a 1:1 ratio of GOC to LOC. This ratio varied between 0:1 to 1:1 during experimental trials.

The stock culture was fed 12 hours before each experiment. This insured that the inoculum would be active at the start of the experiment. Shake flasks (250 ml) containing a total volume of 50 ml each were used. The shaker speed was 250 RPM. This volume and shaker speed were chosen to provide sufficient oxygen transfer.

All experimental solutions contained the following:

- 500 mg C/l as LOC
- 5% by volume buffer (1 M KH_2PO_4 and 1 M K_2HPO_4 mixed to obtain pH ~ 7)
- 625 mg/l $(\text{NH}_4)_2\text{SO}_4$
- 200 mg/l $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
- 9.375 mg/l $\text{CaCl}_2 \cdot \text{H}_2\text{O}$
- 350.0 mg/l $\text{MnSO}_4 \cdot \text{H}_2\text{O}$
- 625 mg/l $\text{FeCl}_3 \cdot \text{H}_2\text{O}$

Initial glucose concentration was varied between 0 and 1250 mg/l. Initial inoculum concentration was varied between 5 and 20 percent, by volume. It was determined that pH must be buffered to between 7.0 to 7.9 during experimentation. Samples were taken at the beginning and conclusion of each experiment.

Samples were analyzed for GOC, TOC, OD, volatile fatty acids, ammonia and nitrogen.

Typical experimental results are presented in Table 2. All glucose present was utilized during microbial degradation. Microbial growth was proportional to initial glucose concentration. Glucose was required for cell growth to occur. Variations in glucose concentration did not enhance degradation of organic species in the leachate or extract. Further, varying inoculum concentration did not influence degradation of organic species in the leachate or extract, either. TOC reduction for typical test cases was approximately 50 percent. TOC reduction did not result exclusively from reductions in volatile fatty acid concentration.

SOIL-BASED MICROBIAL TREATMENT OF LEACHATE

Laboratory soil column experiments were conducted to examine the ability of mixed microbial populations in soil to biodegrade leachate from the lagoon. Biodegradation has been demonstrated to occur sequentially through aerobic and anaerobic microbial metabolic processes [1]. Aerobic processes dominate near the surface of the soil column, where diffusion of oxygen from the atmosphere drives the gradient. Anaerobic processes dominate at increased depths, where oxygen is depleted through aerobic respiration. Data obtained from laboratory scale investigations are readily extrapolated to field responses [2,3].

Factors examined were packing type and influent TOC concentration. These factors directly influence process variables includ-

ing hydraulic flux, solute adsorption, pH and overall organic carbon reduction. A 2x2 factorial experimental design, with two replications per cell was employed. Nutrients were added to the leachate so that available substrate was the limiting factor for biodegradation. Influent pH was adjusted to between 7 and 7.5, also. Column beds were 3 inches in diameter and 18 inches in depth. Experimental procedures were in consonance with those employed in previous column studies [3].

Two column packing types were chosen. One column packing was a sandy loam. This packing was selected based on previous experience with a similar soil. The second column packing was the same sandy loam mixed thoroughly with 30x140 mesh granular activated carbon (GAC), at a soil to GAC ratio of ten to one, by weight. Activated carbon was employed to enhance solute retention time through increased adsorption. Increased column permeability resulted from the addition of GAC, also.

The second factor examined was influent TOC concentration. Influent organic carbon concentration directly affects the extent and rate of microbial growth. If this growth becomes excessive, formation of excessive bioslime may occur, decreasing column permeability. The rate of bioslime formation is not necessarily directly proportional to influent TOC concentration [1]. It is possible that increased influent TOC concentration results in decreased bioslime growth, without affecting overall TOC removal. Therefore, two influent leachate concentrations were employed. Column influent was nominally either full or half-strength leachate.

Experimental results are summarized in Table 3. One representative response for each experimental condition is provided; replication within experimental test conditions was excellent.

Column packing had considerable influence on hydraulic flux. Columns packed with the soil and GAC mixture exhibited an average hydraulic flux almost four times that of columns packed with the sandy loam only. Within packing types, hydraulic response was independent of organic loading.

Columns packed with soil only displayed decreasing hydraulic flux as the experiment progressed. Eventually these columns became plugged for prolonged periods. This probably resulted from formation of an extensive microbial bioslime, especially near the surface of the column. A second contributing factor may have been a sodium-calcium imbalance in the soil. Columns packed with the soil-carbon mixture exhibited relatively constant hydraulic fluxes throughout the experiment.

The most significant measure of treatment effectiveness is cumulative TOC removal. It is the difference between the total influent TOC mass and the total effluent TOC mass integrated over the duration of the column operation. It accounts for both concentration and hydraulic flux variations. TOC removal on a cumulative mass basis for representative columns is presented in Figure 4.

On a cumulative mass basis, columns receiving full-strength leachate removed approximately twice as much organic carbon as those receiving half-strength leachate,

within the same packing. Thus, for a particular packing, the overall mass of TOC removed was directly proportional to the influent TOC concentration, given similar hydraulic fluxes. However, at each influent TOC concentration, columns packed with the soil-carbon mixture removed more than three times the organic carbon removed by those packed with soil only. This resulted primarily from differences in hydraulic flux. In all cases the overall percent organic carbon removal was in excess of 90 percent.

CONCLUSIONS

Controlled, forced extraction of the sludge-filled lagoon appears to be a favorable process for increasing the rate of removal of organic species from the lagoon. Extraction with 0.001 N aqueous sodium hydroxide solution results in high extractant TOCs without excessive TDS. Aerobic microbial treatment of the resultant wastewater stream achieves approximately 40 to 50 percent reduction in TOC. TOC reductions in excess of 90 percent can be achieved through treatment with a soil-based, sequential aerobic/anaerobic system.

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Disclaimer

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TABLE 1. SEQUENTIAL EXTRACTIONS OF SLUDGES

Sequential Extractions: Extractant/Sludge ratio: 2:1

Extractant: 0.001N NaOH (pH = 11)

	Extract	pH	TDS		mg/l	TOC	
			g/l	Σmg/g wet		ΣmgC/g wet	
Primary Sludge	1	8.2	1.92	3.85	124	0.25	
	2	7.9	0.81	5.47	93	0.43	
	3	8.0	0.92	7.31	70	0.57	
	4	8.2	0.44	8.18	56	0.69	
Secondary Sludge	1	11.9	9.34	18.67	3126	6.25	
	2	12.0	4.81	28.29	1275	8.80	
	3	12.1	3.50	35.29	549	9.90	
	4	12.1	1.88	39.04	243	10.30	

TABLE 2. AEROBIC MICROBIAL DEGRADATION OF LEACHATE

	Initial Glucose Concentration (mg/l)					
	0	250	500	750	1000	1250
pH						
initial	7.50	7.50	7.50	7.50	7.50	7.50
final	8.56	8.41	8.31	8.25	8.14	7.98
OD						
initial	2.37	2.47	2.47	2.40	2.34	2.37
final	2.40	3.10	3.60	4.00	4.40	4.85
TOC (mg/l)						
initial	195	279	399	489	593	707
final	136	143	146	139	137	133
GOC (mg/l)						
initial	0	68	168	268	372	488
final	0	0	0	0	0	0
LOC (mg/l)						
initial	195	211	231	221	221	219
final	136	143	146	139	137	133
% Reduction	30.2	32.2	36.8	37.1	38.0	39.3

TABLE 3. LABORATORY SOIL COLUMN RESULTS

	Column #2	Column #3	Column #7	Column #8
Packing Type	Soil+GAC	Soil+GAC	Soil Only	Soil Only
Leachate Feed	Half-strength	Full-strength	Half-strength	Full-strength
Influent TOC (mg/l)	350	700	350	700
Average Hydraulic Flux (l/sqm/day)	28.2	28.2	7.8	7.8
Average TOC Reduction (g/sqm/day)	11.1	22.0	3.5	6.7
Overall TOC Removed (%)	94.2	93.8	97.7	97.3

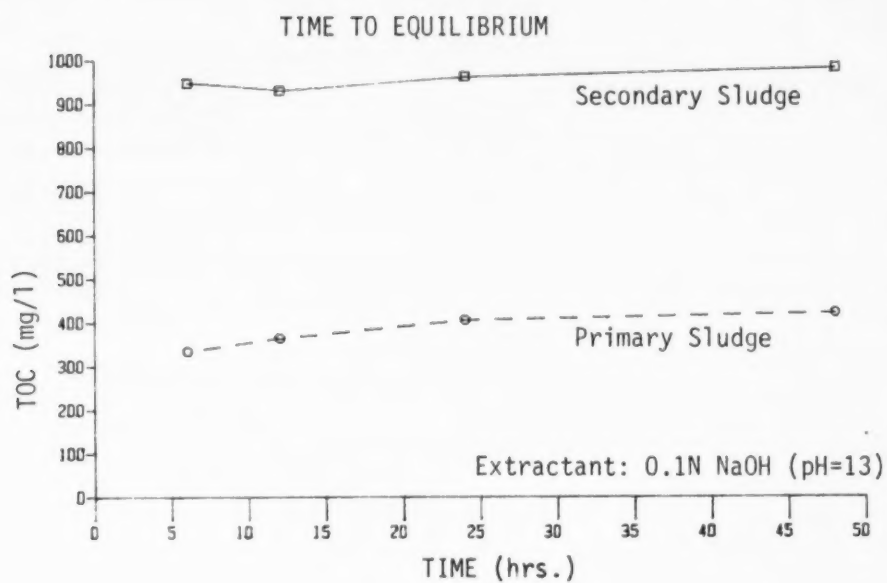


Figure 1

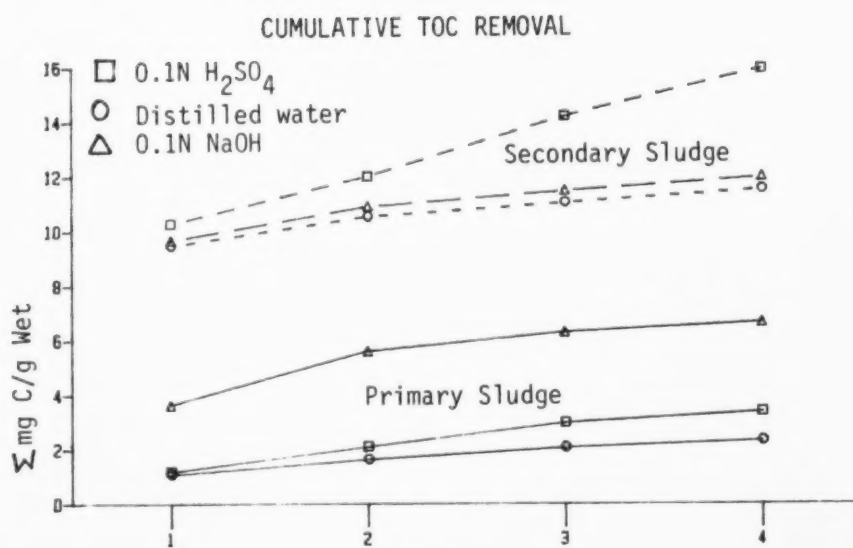
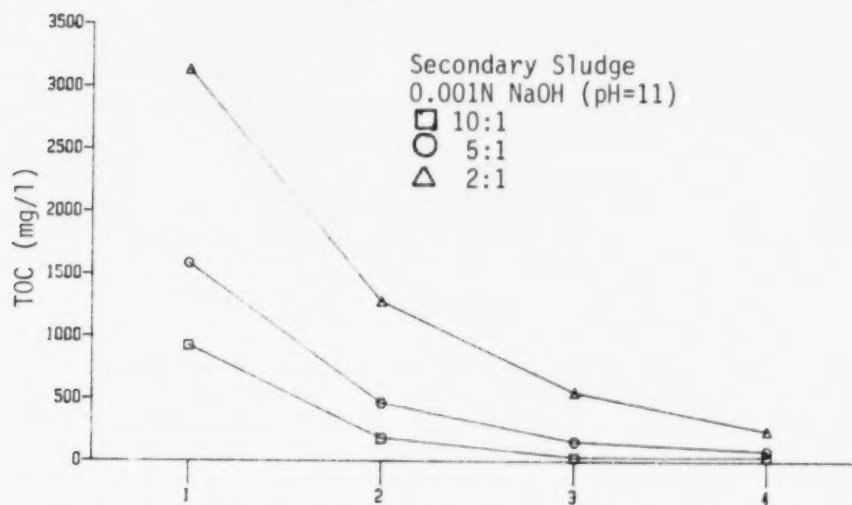


Figure 2

Extractant Volume/Sludge Mass Ratio



Extract
Figure 3

CUMULATIVE TOC REDUCTION (Integrated mass basis)

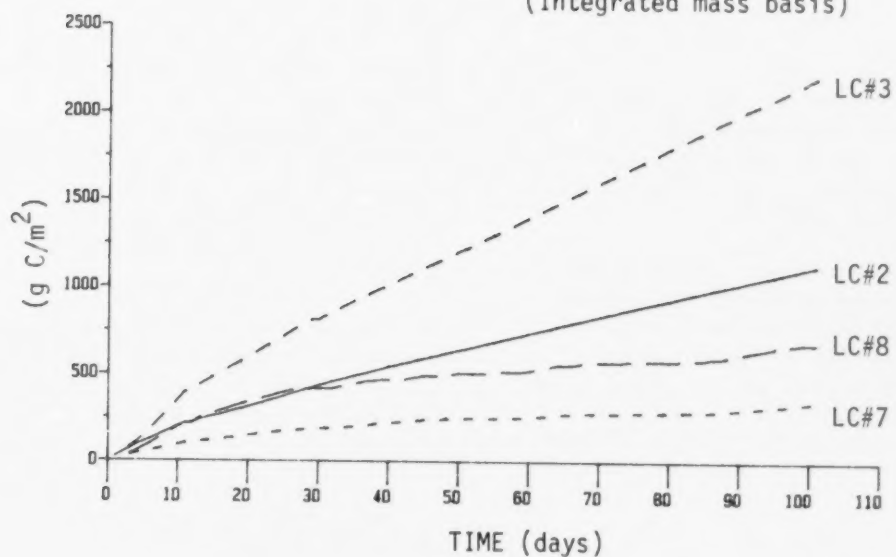


Figure 4

POTENTIAL USE OF ARTIFICIAL GROUND FREEZING
FOR CONTAMINANT IMMOBILIZATION

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ABSTRACT

This paper summarizes a preliminary investigation of the potential use of ground freezing technology for contaminant immobilization. Freezing and thawing were found to significantly decrease the volume of soil slurry and increase the permeability of soils. Frozen metal-contaminated soils eliminated metal leaching to groundwater under the site. Freezing and thawing soils contaminated with moderately volatile organics significantly reduced the soil concentrations of these organics. Freezing the soil from the bottom apparently enhanced upward movement of the organics to the soil surface where losses occurred by volatilization. The amount lost depended on the mobility of the specific volatile component and was as high as 90% for chloroform, benzene and toluene and as low as 45% for tetrachloroethylene. Input to groundwater during freezing and thawing of these organics was much less than the unfrozen (control) treatment. Artificial ground freezing for decontamination of soils and for immobilization of contaminants is now being tested on a larger scale.

INTRODUCTION AND PURPOSE

Hazardous waste treatment and disposal is one of the major environmental concerns facing industrialized countries. Transport of contaminants to ground and surface water is probably the main issue. Neely et al. (11) reviewed available techniques for remedial action at uncontrolled hazardous waste sites and concluded that current techniques are not adequate for protecting ground and surface water. EPA (4) also reviewed in-place treatment techniques and concluded that the available methods include

extraction, immobilization, degradation, attenuation and reduction of volatilization. Immobilization methods include slurry walls, grout curtains and physical removal of contaminated soils to properly designed sites. In some cases the nature of the slurry prevents its physical removal by mechanical means.

The purpose of this paper is to report on the potential use of artificial ground freezing to immobilize contaminant transport in soils and in-place treatment of hazardous waste sites.

APPROACH

Ground Freezing Technology

Artificial freezing is not a new concept. It has been used for dewatering sludge (1,2,3,5), for desalting sea water (6,7,13), and for constructing mines and tunnels and other civil engineering projects. Iskandar and Houthoofd (8) reviewed the literature pertinent to those projects and discussed the concepts of artificial ground freezing.

When the soil is initially subjected to subfreezing temperatures, soil water starts to freeze and ice lenses begin to form. Chemicals in the soil water are excluded from the ice, so they become concentrated in the remaining soil solution. The chemicals accumulate either in pockets or in thin liquid films around the particles. As the temperature drops further, the amount of ice becomes larger and the amount of unfrozen water decreases. The permeability of the frozen soil is substantially less than in the unfrozen soil. However, after the soil thaws, its permeability increases to a higher value than prior to freezing. In addition, soil strength increases significantly upon freezing compared to unfrozen soil. The potential use of ground freezing for immobilizing contaminants is based on the low permeability and high strength of frozen soils.

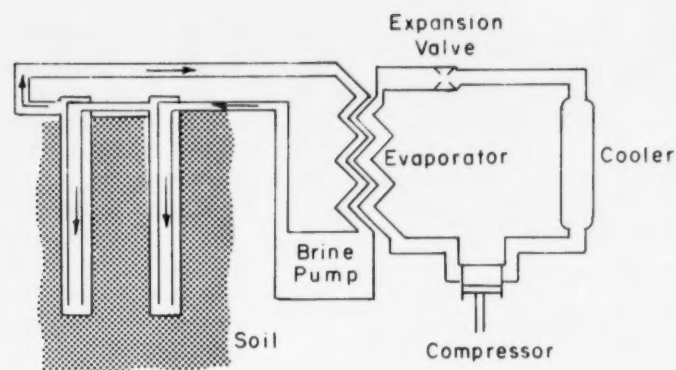
Hardware for Ground Freezing

Artificial ground freezing is usually done using the Poetsch method (14). Essentially, vertical drill holes with standard steel

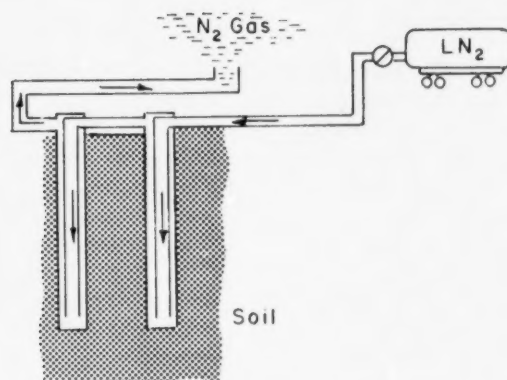
casings are uniformly spaced along the desired line. Common bore diameters range from 3 National Pipe Standard (NPS) to 6-NPS. Standard black iron pipes, one-half the bore diameter, are inserted in each drill hole, forming concentric cylinders. A header or manifold system provides coolant to the interior pipe, with the return line being the outer casing. The manifold is insulated and connected to the freeze pipes with insulated pipes to reduce thermal losses. A self-contained refrigeration system pumps coolant around the freeze loop. Temperature measuring instrumentation is appropriately placed for monitoring the progress of the freeze front.

Two types of coolants have been used in artificial freezing projects: low-temperature ethylene glycol brine and liquid nitrogen (LN_2). Brine is less costly and is recyclable, but the time needed to freeze the soils is much longer than with LN_2 . A uniform freezing front can be achieved with brine coolant but not with LN_2 . On the other hand, LN_2 is more desirable in situations where there are very high concentrations of chemicals that require a much lower temperature to freeze (lower than $-55^\circ C$), and in emergency situations where time is of the essence. Figure 1 shows schematic diagrams of the brine and the LN_2 methods.

Sullivan et al. (14) discussed the factors involved in artificial ground freezing for containing hazardous waste and the cost associated with each factor. Information on the quantity, quality, toxicity and solubility of the chemicals is needed, as well as temperature, soil, geology and groundwater data.



a.



b.

Figure 1. Artificial ground freezing by brine (a) and liquid nitrogen (b).

Using a computer program and published cost data, they concluded that the time required for soil freezing plays an important role in the overall costs. The time factor depends on characteristics of the site such as soil water content, soil texture, groundwater depth and flow, soil chemistry, temperature and precipitation. Most of this information is routinely collected during site investigations.

Experimental Method

Plexiglass columns (Figure 2) 12.5 cm in diameter and 80 cm in height were filled with dredge material from Green Bay, Wisconsin, after spiking with either heavy metals or semivolatile organics. The PH of the material was 7.0 and oxidizable organic mater was 4.70%. The metals added were Cd, Zn, Cu and Ni in concentrations ranging from

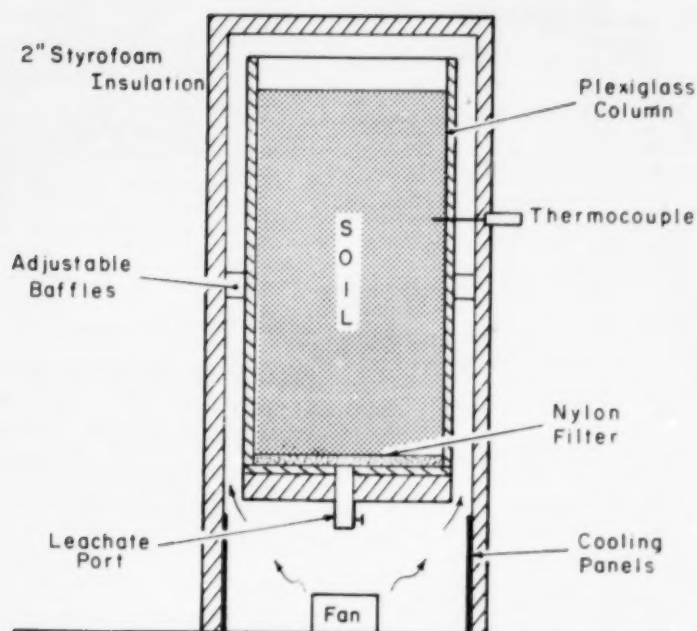


Figure 2. Experimental setup.

400 to 800 $\mu\text{g/g}$ dry soil. The organics included chloroform, benzene, toluene and tetrachloroethylene in concentrations ranging from 40 to 45 $\mu\text{g/g}$ dry soil. The water content of the sediment prior to freezing was 160-170% w/w on a dry weight basis. Control treatments (no chemicals added and/or no freezing/thawing) were included for comparison. The columns were instrumented with thermocouples to measure the soil temperature at depth. Leachates as a result of gravity flow were collected and metered during the thawing period, and subsamples were analyzed. No water was added to the columns during the experiments. At the conclusion of the experiments, soils were sectioned and subsamples were analyzed. Metals were analyzed by Inductively Coupled Plasma (ICP) and organics were determined by extraction with tetraglyme and

analysis on a gas chromatograph-mass-spectrometer (HP 5992 GC-MS) equipped with a purge and trap sampler (HP 7675A). Deuterobenzene (C_6D_6) in tetraglyme was added to each sample as an internal standard just prior to purging.

Freezing the soil was conducted gradually and freezing direction was from the bottom up. The soil temperature during freezing ranged from -1.8° to -16.0°C . The rate of frost penetration was recorded using a thermocouple array and a data logger.

RESULTS

Consolidation

Figure 3 shows the vertical distribution of soil water content in selected frozen, unfrozen and

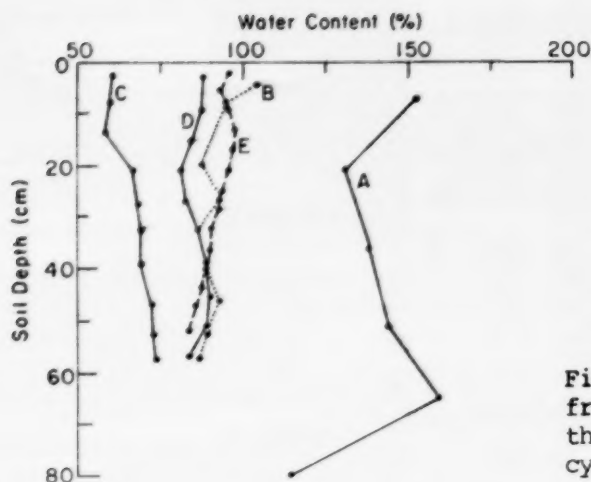


Figure 3. Soil water content in the frozen treatment (A), after one freeze-thaw cycle (B, D), three freeze-thaw cycles (C), and unfrozen treatment (E).

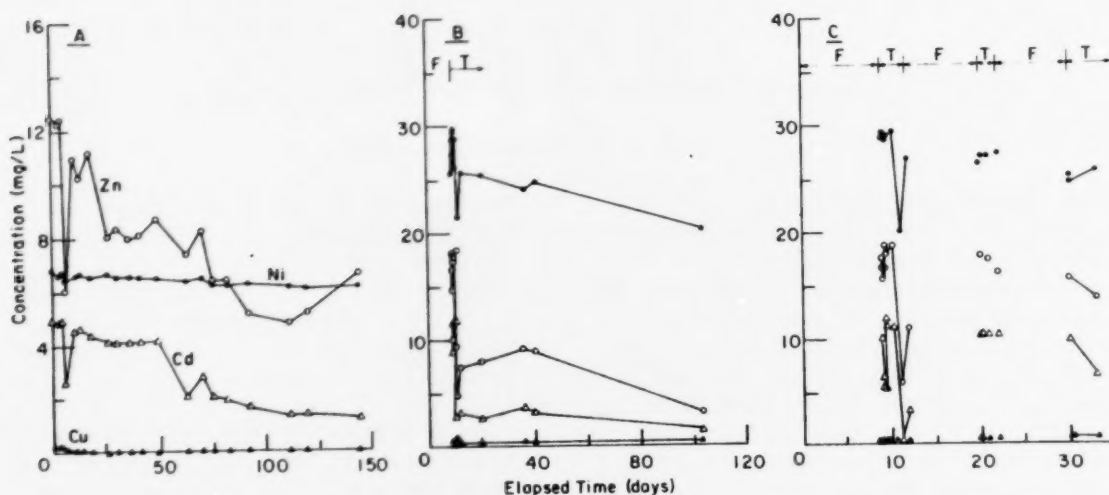


Figure 4. Concentration of heavy metals in leachate from unfrozen treatment (A), after one cycle of freezing (B) and during three cycles of freeze-thaw (C).

frozen-thawed treatments. After 120 days the water content in the unfrozen treatment decreased from 160-170% to 80-95% which is about 60% of the initial conditions. Freezing and thawing the sediments decreased the water content to lower values

than those obtained under natural drainage and in significantly less time. For example the sediment subjected to one cycle of freeze-thaw reached 80-90% water content in about 20 days and the sediment subjected to three cycles of freeze-

thaw reached a water content of 60-75% in 36 days. Because of the time savings, freezing and thawing can be a cost effective way of drying contaminated sediments in lagoons to allow heavy equipment to enter the sites and remove the materials.

Metals

Figure 4 shows the leachate concentration of Zn, Ni, Cd and Cu from the unfrozen sediments and from the frozen-thawed treatments as a function of time. In the leachate from the unfrozen treatment, the metal concentrations were in the following order: $Zn > Ni > Cd > Cu$. In the frozen-thawed treatments, the order of metal concentration was similar, except that $Ni > Zn$. Freezing and thawing sediments apparently increased the amounts of Ni in the soil solution compared to the unfrozen control. In general, most of the metals added to the slurry were sorbed on the sediments. Only a small portion of the added metals was leached. The amounts leached depended on the type of metal and on the number of freeze-thaw cycles. Cu concentrations in the leachate were the lowest of the four. While freezing and thawing increased the amount of Cu in solution, the increase was not substantial. Cd and Zn concentrations in leachates were higher than Cu, and one cycle of freeze-thaw did not increase Cd and Zn concentrations in the leachate. However, three cycles of freeze-thaw (Figure 4) increased the Cd in the leachate from about 5 mg/l to about 7 mg/l and the Zn from 7 mg/l to 15 mg/l.

The mechanisms involved in metal retention by sediments include sorption, precipitation and complex-

ation. Stevenson and Ardakani (12) reviewed the relative stabilities of metal-organic complexes of some trace metals and found at pH 5 they were in the order $Cu > Pb > Fe > Ni > Mn > Co > Zn$. The order of metal concentration in the leachate from the unfrozen column is the reverse of their stability constants. This indicates that metals may have formed complexes with insoluble organics such as fulvic and humic acids. However, freezing and thawing may have increased the solubility of Ni but had little or no effect on the other metals.

Organics

Figure 5 shows the concentration of the volatile organics in the

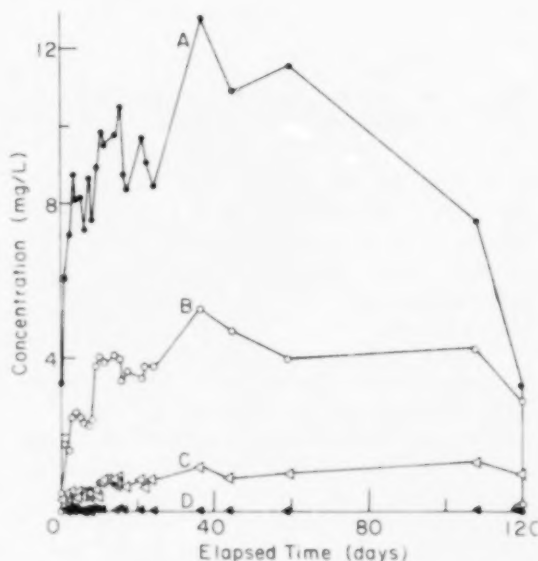


Figure 5. Concentration of chloroform (A), benzen (B), toluene (C) and tetrachloroethylene in leachate from the unfrozen treatment during 120 days.

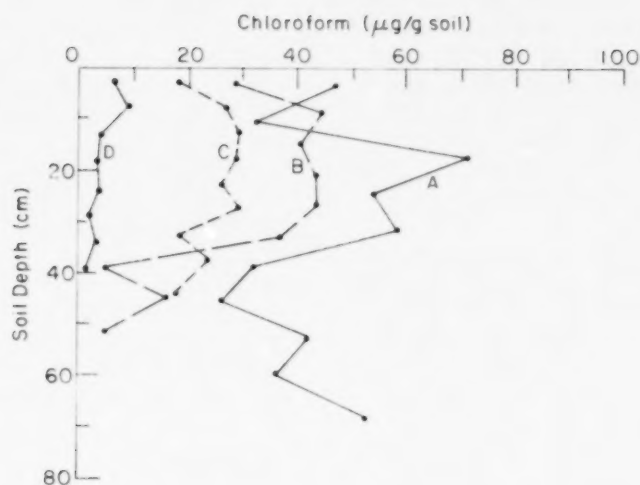


Figure 6. Chloroform concentration in soils kept frozen (A), one cycle of freeze-thaw (B), unfrozen (C) and after five cycles of freeze-thaw (D).

leachates from the unfrozen treatment and from the treatment receiving five freeze-thaw cycles. With the exception of one sample, the order of concentration in both treatments was chloroform > benzene > toluene > tetrachloroethylene. Concentrations of the organics in the leachate were higher from the unfrozen treatment than from the frozen-thawed treatment. This means that freezing and thawing as conducted in these experiments from the bottom up would decrease groundwater contamination for these four organics. The concentration of these organics in the leachates is inversely related to their octanol/water partition coefficients (K_{ow}). These values for chloroform, benzene, toluene and tetrachloroethylene are 93, 135, 490 and 615, respectively (10).

Figure 6 shows the effect of freezing and thawing on the concentration of chloroform in soils. These concentrations were obtained at the conclusion of each treatment. The vertical distributions of benzene and toluene were similar to that of chloroform, and the data are not presented. The vertical distribution of chloroform indicates that the frozen soils contained the highest concentrations. Also, a redistribution of chloroform occurred during freezing. Initially the profile was homogeneous, and the concentration of chloroform was 40.1 µg/g dry soil. The low concentration of chloroform in the frozen soil at some depths may be due to ice lenses, and the high peak concentration (about 70 µg/g) is probably due to rejection upon freezing. The lowest soil

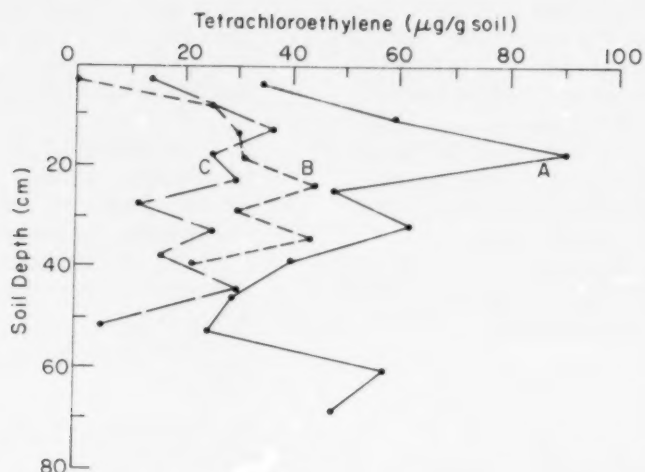


Figure 7. Tetrachloroethylene concentrations in soils kept frozen (A), after five cycles of freeze-thaw (B) and unfrozen (C).

chloroform concentrations were found in the treatment receiving five freeze-thaw cycles. Since the leachate from this treatment contained the least amount of chloroform, it was concluded that chloroform was lost to the atmosphere by volatilization. The data from the columns that received 1, 2, 3 and 4 freeze-thaw cycles support this finding. Jenkins et al. (9) reported on the fate of organics in overland flow soils. They found that decreasing the temperature from 25.7°C to 2.5°C decreased the rate of soil and plant removal of these organics. However, they did not test the effect of freezing and thawing. It seems that soil freezing from the bottom of the columns caused upward movement of organics and their accumulation in the soil surface in high enough concentrations to enhance the flux to the atmosphere. Upon thawing, downward movement of organics may have oc-

curred, particularly through the macropore channels formed during freezing and thawing.

The effect of freeze-thaw on tetrachloroethylene in soils (Figure 7) was similar to the other three organics except that the atmospheric loss of tetrachloroethylene was less. This may be due to the stronger binding of tetrachloroethylene with soil constituents as evidenced by its higher K_{ow} value of 615 compared with 93, 135 and 490 for chloroform, benzene and toluene, respectively.

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

WASTE DISPOSAL BY HYDROFRACTURE AND APPLICATION OF THE TECHNOLOGY TO THE MANAGEMENT OF HAZARDOUS WASTES

by

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A unique disposal method, involving hydrofracturing, has been used for management of liquid low-level radioactive wastes at Oak Ridge National Laboratory (ORNL). Wastes are mixed with cement and other solids and injected along bedding plane fractures into highly impermeable shale at a depth of 300 m forming a grout sheet. The process has operated successfully for 20 years and may be applicable to disposal of hazardous wastes. The cement grout represents the primary barrier for immobilization of the wastes; the hydrologically isolated injection horizon represents a secondary barrier. At ORNL work has been conducted to characterize the geology of the disposal site and to determine its relationship to the injection process. The site is structurally quite complex. Research has also been conducted on the development of methods for monitoring the extent and orientation of the grout sheets; these methods include gamma-ray logging of cased observation wells, leveling surveys of benchmarks, tiltmeter surveys, and microseismic arrays. These methods, some of which need further development, offer promise for real-time and post-injection monitoring. Initial suggestions are offered for possible application of the technology to hazardous waste management and technical and regulatory areas needing attention are addressed.

INTRODUCTION AND PURPOSE

At Oak Ridge National Laboratory (ORNL), low-level radioactive wastes are routinely disposed of by a process termed "hydrofracture." The liquid wastes are mixed with cement and other solids to form a slurry that is pumped under pressure through an injection well into underlying strata. The slurry follows fractures in the strata and sets to form a solid grout, which contains and immobilizes the radioelements.

This process has been successfully developed at ORNL over the last quarter century. Initial development work was performed at test facilities; in the mid-1960s, the process became operational. A

new injection facility was put into operation in 1982. A total of over 1.5 million curies of radioelements has been disposed of; the principal nuclides are Sr^{90} and Cs^{137} , although others, including H^3 , Co^{60} , Ru^{106} , and isotopes of U, Am, and Pu, also occur in the wastes. This process represents the only permanent geologic disposal of nuclear wastes in the United States.

The disposal operation is unique and is based on the common practice of hydrofracturing, which is routinely used by the petroleum industry to increase porosity and permeability in reservoir rocks by fracturing the rocks with water injected under pressure. It appears that this technique may have potential application

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to the management of some kinds of hazardous wastes, especially if alternative methods to shallow land burial are sought. Thus, our purpose is to discuss the basic principles of the hydrofracture program at ORNL and to offer initial thoughts on the application of the technique to hazardous waste management.

THE HYDROFRACTURE PROCESS

A complete review of the history of the hydrofracture operation and a description of the process can be found in previously published works (1-3). The process is a large-scale batch operation (Fig. 1). Liquid wastes are stored in

is slotted at a depth of approximately 300 m. Fractures in the host rock, a shale of low permeability, are initiated along bedding planes by pumping a few thousand liters of water into the well; this is followed immediately by the slurry, which spreads radially from the injection well along the fractures. The slurry sets to form a thin (less than a few cm) grout sheet that extends up to several hundred meters from the well. No grout sheet has been detected more than 220 m from the injection point. Later injections are made through slots cut at shallower depths in the well, thus allowing maximum use of the host injection strata.

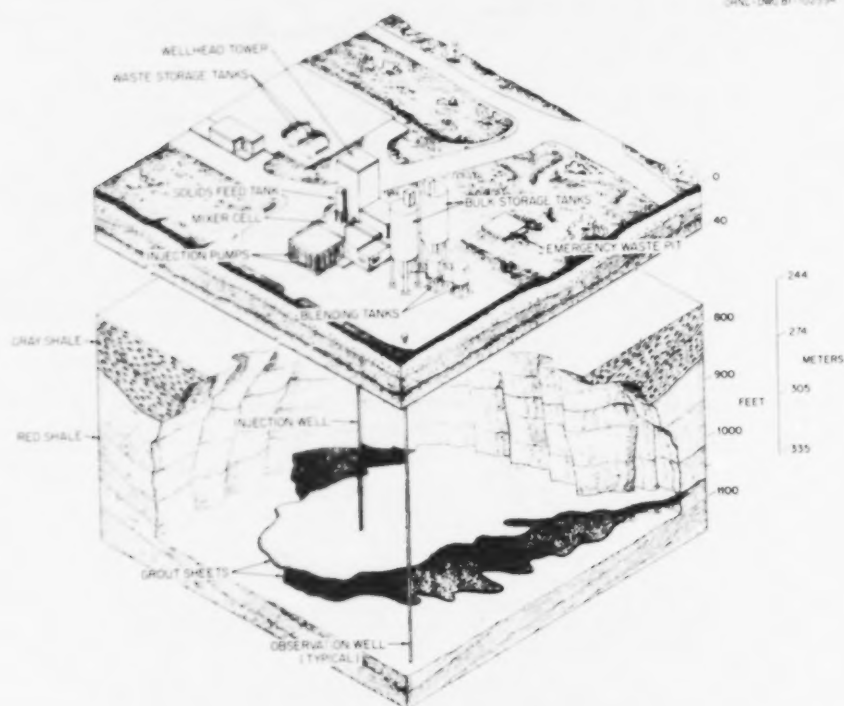


Figure 1. Conceptual drawing of the Hydrofracture Facility at Oak Ridge National Laboratory. Surface facilities, the injection well, one cased observation well, and grout sheets are depicted.

underground tanks and disposed of typically every one to two years. The waste solutions, which are alkaline and 1-2 M NaNO_3 , are blended with cement and other additives to form a slurry, which is pumped under approximately 20-MPa pressure into the cased injection well. The casing

Disposal is normally done over a two-day period in two eight- to ten-hour shifts. The total volume disposed of ranges from 350,000 to 700,000 l. Although some operational problems have arisen over the years, the technique has been highly successful. A major reason

for this success is that the engineering and operational aspects of this technique are not unique but rather are standard practice in the petroleum industry.

The costs for disposal at ORNL are approximately \$0.30/l. About half of this is operational cost, including dry solids and personnel. The other half represents amortization of the capital cost (\$5.4 million) of the facility prorated for disposal of 40×10^6 l of waste. The costs are sensitive to process parameters (batch size, injection rate, etc.), which were chosen to fit ORNL requirements.

PRINCIPLE OF WASTE ISOLATION

The basic objective of the ORNL hydrofracture program is to effectively isolate the wastes from the accessible environment. This is achieved through immobilization of the wastes in a variety of ways. The cementitious waste carrier is the primary barrier and is tailored to retard the two principal isotopes that occur in the wastes, Sr^{90} and Cs^{137} . Highly sorbing illitic clay is added to help retain the Cs^{137} . Most of the Sr^{90} occurs as a fine-grained precipitate in the waste; this precipitate is physically entrapped in the cement and Sr^{90} is largely immobilized in this fashion. The secondary barrier is the shale, which has a high content of illite. If isotopes such as Cs^{137} should escape the grout, they should readily be sorbed by the shale. Equally important is the fact that the 100-m-thick host shale formation is of low permeability, contains small amounts of groundwater, and is removed from any fresh-water aquifer by over 100 m of intervening strata.

One of the most significant aspects of the waste isolation operation at ORNL is the generation of bedding plane fractures. It is critical that the radioactive slurry remain in the impervious host horizon and not travel through vertical fractures into strata that might have hydrologic communication with the environment. As noted later, the great mechanical anisotropy of the shale and the fact

that the injections are apparently shallow enough so that the least principal stress is vertical are factors that cause the nearly horizontal bedding plane fractures. The production of fractures with this orientation represents one of the most significant differences with the standard hydrofracture methods used in industry, where the fracturing is done at much greater depths with the intent of producing vertical fractures that cross many strata.

SITE SELECTION CRITERIA

Idealized Criteria

A set of idealized geologic criteria that should be considered in selecting a site for a hydrofracture facility has been developed (2,3). The criteria are similar to many used in the selection of repository sites for high-level commercial nuclear wastes (4). For instance, a properly located hydrofracture site should be in an area that is tectonically stable (low frequency of earthquakes, no volcanic activity or recent faulting, low rates of uplift) and has few, if any, natural resources that might be sought in the future. The injection horizon should be thick and laterally extensive enough to contain and to help isolate the wastes, and it should be hydrologically isolated from the accessible environment. The host strata and waters contained within should have geochemical characteristics that enhance immobility of the wastes through retardation, precipitation, or formation of colloids, and should produce horizontal (or nearly horizontal) bedding plane fractures.

Characteristics of the ORNL Site

The site at ORNL, although selected prior to systematic identification of these idealized siting parameters, conforms to them fairly well. A detailed description of the site geology has been published by Haase et al. (5). The injection horizon is the Pumpkin Valley Shale, which is a formation in the Lower Paleozoic Conasauga Group. The shale is

highly impermeable (0.01 - 0.001 millidarcy [1,2]), approximately 100 m thick, highly sorbing for some nuclides, well bedded, and can be easily fractured along bedding planes. The area is tectonically stable and does not contain known mineral or energy resources.

Structurally, the site is quite complex. It lies on the leading edge of the Copper Creek fault, a major thrust fault in the Valley and Ridge Province; a number of inactive cross-strike tear faults occur within hundreds of meters of the facility. The Pumpkin Valley Shale dips at 15 to 20° and contains common small tight folds; it is well jointed, and bedding plane slippage has occurred during deformation. The joints appear to be the controlling factor in groundwater movement. In spite of the complexity of the site geology, it does not appear to have had any detrimental effect on the successful disposal operations at the site.

A program is currently under way to more fully clarify the subsurface hydrology of the site. Deep (500-m) monitoring wells have been drilled, and hydrologic testing of the injection horizon and other strata is under way. Recent work (6) shows that groundwaters from the injection horizon and surrounding strata are highly saline, containing up to 190,000 ppm total dissolved solids. The dominant constituents are Na, Mg, Ca, and Cl. The salinity decreases upward in the wells. No age data are yet available on the groundwater.

DEVELOPMENT OF MONITORING PROCEDURES

Monitoring Methods

It appears certain that if the hydrofracture technique is to be considered for future disposal operations, including disposal of hazardous wastes, sensitive and accurate monitoring schemes must be developed and applied so that the distribution and fate of the wastes can be understood. When the ORNL injection facilities were constructed, cased observation wells were installed between 30 and 100 m from the injection well. These

observation wells intersect the injection zone and are logged with a gamma-ray detector after each injection. By comparing the gamma-ray profiles between injections, it is possible to determine the depth and orientation of a grout sheet and get some general information on its extent (1-3).

During a series of recent bimonthly injections, research was conducted on the development and application of ground deformation and microseismic surveys as monitoring techniques. Recent articles (7,8) describe these techniques. The ground deformation approach is based on the principle that subsurface fractures produced by hydrofracturing create a measurable deformation at the surface. The shape of this deformation reflects the orientation of the fracture (9,10). Two methods have been examined for measurement of ground deformation at ORNL: (1) precise leveling of benchmarks and (2) tiltmeter surveys.

Precise Leveling

Leveling surveys have been conducted for eight recent injections. A total of 75 benchmarks up to 700 m from the injection well were surveyed before and after each injection. For the October 1983 injection, a fairly representative one, deformation is characterized by uplift of up to 2.5 cm; the area of maximum uplift is slightly south of the well. Such a configuration indicates that the fracture rises to the north along the dip of the shale. This orientation is expected, as it is in the direction of least lithostatic pressure and along bedding planes. The orientation can be confirmed by the gamma-ray logs from the observation wells. A leveling survey taken 30 days later showed that the uplift had decayed to approximately 50 percent of its initial value and had shifted slightly to the north. Surveys from other injections are similar, but the shape of the surface deformation may vary.

Tiltmeter Surveys

A series of eight tiltmeters was installed in shallow wells 125 and 200 m laterally from the injection point to measure ground deformation during the October and November 1983 injections. The instruments are capable of detecting injection of the first few thousand l of water, and they accurately recorded the uplift and deformation throughout the injections. During the 30-day period after the October injection, a subsidence of the uplift was recorded, corresponding closely with the leveling data. Modeling of the tiltmeter data, in an effort to determine the orientation of the subsurface fracture, however, has not produced an orientation that corresponds with actual measurements from the gamma-ray logging. Currently used models are for homogeneous, isotropic media; the stratigraphy at the ORNL site is highly heterogeneous and anisotropic. Work is continuing to more fully refine the models.

Microseismic Arrays

A third method of instrumental monitoring involves detection of microseismic signals associated with the injection. This approach is based on the principle that the fracturing process should produce seismic signals; with properly placed geophones, it should be possible to monitor the fracture as it propagates. Thus far, this effort has provided useful information on the mechanisms of fracture formation and has shown that seismic activity continues for weeks after an injection. These data indicate that the strata overlying the injection zone undergo mechanical relaxation after the induced stress of an injection. The microseismic method has not yet been developed at ORNL for determination of the extent and orientation of the fractures.

Overview

There is considerable work yet to be done on development of monitoring techniques, especially those that provide real-time data during an injection. The

two methods that do provide such data (tiltmeter, microseismic) show promise; of the two, the tiltmeter method appears to be better developed at present. Stow et al. (7) provide a relative evaluation of the techniques. While it is anticipated that future hydrofracture disposal operations may require installation of real-time monitoring systems, absolute techniques, such as gamma-ray logging, will probably also be required.

CONSIDERATION OF HYDROFRACTURING FOR HAZARDOUS WASTE MANAGEMENT

In this final section, two general topics will be addressed: (1) ways in which the hydrofracture method might be used for some types of hazardous waste management, and (2) technical and regulatory aspects that need to be addressed if the method is applied to hazardous waste.

Use of the Technique for Hazardous Wastes

It is felt that the hydrofracture technique may have significant potential for disposal of certain types of hazardous wastes. Because the operational aspects of the disposal operation are fairly routine, attention is directed here toward waste forms and carriers that are compatible with the injection process and the host formations.

It may be possible to use the method for disposal of certain heavy metals. For instance, chromium could be precipitated as the highly insoluble sulfate, or other transition metals might be fixed by chelating agents. The insoluble salts or chelated metals could then be mixed with a cementitious carrier and injected. Cement might also be useful as a carrier for PCBs.

There is no reason why materials other than cement might not be considered as waste carriers. Polyacrylamide grouts might prove to be chemically compatible with certain wastes and thus offer sufficient isolation potential. Alternatively, phenol or amine polymers might be developed as waste forms and carriers that

could be pumped into an injection zone before polymerization.

For certain wastes, it might be feasible to produce a microencapsulated waste form that could be mixed with cement or an organic-based carrier for disposal. The costs of microencapsulation would probably dictate use of such a method for only a limited number of very toxic wastes. Particle size should probably be kept below 1 mm.

Technical and Regulatory Considerations and Needs

If the ORNL hydrofracture technique is considered for permanent disposal of hazardous waste, the existing technical data base is inadequate to provide assurance that the process is environmentally safe, as determined by current statutes. There are a number of technical areas that must be pursued to provide the data that will be required for use of the technology. Because one of the principal factors in waste isolation by this method is the creation of (nearly) horizontal bedding plane fractures and because little is known of the behavior of such fractures in rocks, research must be directed toward fracture behavior in anisotropic media. This and other critical rock mechanics issues relative to hydrofracturing are discussed by Doe and McClain (11). A related issue is the determination of the maximum volume that can be injected into a single well.

Work must also be continued on development and refinement of real-time monitoring techniques. Such monitoring is critical to ensure that fractures that form during disposal do not break a containment horizon and intersect horizons that are connected to the accessible environment.

Finally, research should be directed toward study of the long-term stability of the injected hazardous waste. Groundwaters at injection depths may be highly saline and have corrosion and complexation potential. The long-term interaction of

such waters and wastes should be understood.

It is also appropriate to note the need for consideration of the regulatory status of injection wells. Certainly many regulations could apply to a hydrofracture site, including its surface and subsurface facilities. At present, federal underground injection regulations (EPA regulations for the Underground Injection Control Program, 40 CFR 144) and similar statutes at the state level may be applied to the process because the technology involves subsurface injection of wastes. Underground injection regulations are written for disposal of liquids, including hazardous wastes, into porous and permeable aquifers; the wastes mix with non-potable groundwater and slowly disperse. The concept of waste isolation by hydrofracturing, as noted previously, is totally different from the disposal method envisioned by existing legislation. Thus, it may be necessary to formulate legislation that specifically addresses the hydrofracture process.

SUMMARY

The hydrofracture process has been shown to be a viable method for disposal of radioactive wastes at ORNL. The operational aspects are routine and could rather easily be adapted for hazardous waste disposal. Because the process appears to have applicability for hazardous waste disposal, research needs to be conducted on the development of stable waste forms and carriers, as well as on the rock mechanical and monitoring aspects. Site selection considerations are of prime importance in future applications of the technology. There may be a need to more fully explore the regulatory picture because of the fact that existing regulations for deep well injection were not formulated with the concepts of waste isolation that characterize the hydrofracture process.

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DESIGN AND INSTALLATION OF A GROUND WATER INTERCEPTOR/COLLECTION TRENCH AND TREATMENT SYSTEM

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ABSTRACT

This paper presents a case history of a unique ground water cutoff wall, collection and treatment system recently approved by the New York State Department of Environmental Conservation (NYSDEC) and the U.S. Environmental Protection Agency (USEPA). The system is designed to collect and treat ground water contaminated with organics and migrating from a manufacturing facility in Upstate New York. Construction began in late 1984 and on line testing is expected to be complete by March 1985.

Characteristics of the hydrogeology, waste and treatment system will be focused on along with particular hurdles that had to be overcome with respect to design and actual construction. Questions such as: "how clean is clean" and "how much regulatory involvement can be expected" will be addressed.

INTRODUCTION AND PURPOSE

Early in 1984, Dames & Moore was awarded a contract to provide engineering, design and construction management services to install a ground water cutoff wall and treatment system for an industrial client located in upstate New York.

The system was selected and designed by Dames & Moore after completion of a remedial investigation/feasibility study (RI/FS). The RI/FS which consisted of borings and ground water monitoring wells were performed by Dames & Moore during preceding investigations. Appropriate laboratory analysis was performed on selected ground water samples to determine plume migration and concentration characteristics. Using this data, Dames &

Moore performed engineering design and obtained approval by both NYSDEC and the USEPA in approximately nine months.

The purpose of the ground water cutoff wall and treatment system is to intercept, collect and treat ground water containing organic contaminants ranging up to 1,400 ppb that are migrating toward the client's property line. The primary contaminants are trichloroethylene (TCE) and 1,1,1-Trichloroethane (1,1,1-TCE). The system is approximately 1,800 feet long. It consists of a main interceptor drain 900 feet in length; a 900-foot lateral interceptor drain/recharge system; and a temporary organic treatment system which will remain on-line until the client's industrial wastewater treatment facility (IWTF) is upgraded to have the capability

of treating organics. A plot plan showing the location of the interceptor trenches, plume concentrations and direction of ground water flow is shown on Figure 1.

APPROACH

The stratigraphy of the site is generally composed of a silty fine sand stratum varying in thickness from seven feet to greater than 20 feet, overlying a gray silty clay. Along the northwest portion of the site an interbedded layer of brown sandy clay and gray clay is present between the silty fine sand and the gray silty clay. Ground water which is generally encountered about 10 feet beneath the ground surface, is flowing toward the northwest.

The main drain has been aligned such that it is situated directly across the path of contaminated water that is migrating toward the property boundary as shown on Figure 1. The main interceptor trench shown on Figure 2 has been keyed into the silty clay unit at the bottom of the upper aquifer. Figure 3 shows a cross section of the trench and the basic construction of the drain. The design includes a 6-inch perforated PVC pipe in a bed of filter stone and a geotextile fabric drain that intercepts the ground water and diverts it toward the filter stone and drainage pipe. The fabric drain is sandwiched between a geotextile filter fabric which extends around the filter stone to keep silt and fines from clogging the system. The advantage of this unique fabric drain is that it significantly reduces the amount of compacted filter stone required above the drainage pipe. It also allows the use of excavated material as backfill. The alternative, offsite disposal, would have been very costly as extensive testing and transportation to a secured landfill would be required. The main drain also includes five manholes, two of which (at the lowest elevations) include sump

pumps to pump the intercepted water to the temporary treatment plant.

In addition to the main drain, the system also includes a lateral interceptor drain and recharge system, shown on Figure 4. It has been aligned such that it runs through the center of the plume along the axis of highest concentration of contaminated ground water. The purpose of the lateral is to speed up the cleanup process by intercepting the most highly contaminated water and by recharging clean water into the aquifer after the aquifer has been sufficiently dewatered. Recharging clean water in such a manner increases the hydraulic gradient and hence the flow and velocity of residual contaminated water toward the main interceptor drain where it is collected. This in effect, increases the number of flushings of the aquifer to remove residual contaminants that may be adhering to soil particles. The basic design is the same as for the main interceptor drain. However, the drain is located a few feet above the silty clay unit and several feet below the top of the seasonally high ground water table. As a result, no impermeable liner is required beneath the drain. This configuration enables it to serve the dual purpose of draining the ground water when the water table is high and recharging the aquifer with fresh water when the water table drops. To provide recharge capability, a shutoff valve is located in the manhole where the lateral has been hooked up to the main interceptor drain. Additionally, a metered connection was made to the plant's city water line to recharge water through a manhole into the lateral. Thus, during periods of low water table such as the summer months or when the aquifer has been sufficiently dewatered, the shutoff valve can be closed and the metered connection at the manhole can be turned on, to permit recharge to enter the soil through the lateral interceptor/recharge pipe.

Installation of the interceptor/collector pipe required excavation to depths of 15 to 25 feet below grade and approximately 10 feet below the water table. Space was limited and, therefore, a sheeting box was used to brace all cuts. Due to the nature of the ground water, treatment of all dewatering discharge was mandatory. To accomplish this, a temporary organic treatment system, capable of treating up to 70 gpm during construction, was built nearby. Water from the excavation was pumped into the system, treated, and discharged into a local storm sewer. The treatment system consisted of seven Calgon "Disposorb" units which contain granulated activated carbon (GAC) connected in a parallel mode. Each Disposorb unit is capable of treating up to 10 gpm of ground water containing up to 50 ppm suspended solids at pressures not to exceed 7.5 psig. This configuration is shown on Figure 5. Appropriate pressure regulators and volumetric flow valves were also installed to regulate the system within the manufacturer's suggested range. Prefiltration was achieved through the use of three bag filters. The entire system was enclosed in a heated structure.

On occasions where more than 70 gpm was encountered in the deep cut, tanker trucks were used, in addition to the temporary organic treatment system, to handle dewatering discharge. The trucks would empty their loads into a holding tank at a nearby industrial waste treatment facility, which was also equipped with GAC units for organic treatment.

Construction proceeded in an uphill direction starting with the lowest manhole, under the continuous inspection of a NYSDEC field representative. Periodic measurements of volatile organics in the air within the trenches were obtained by both NYSDEC and Dames & Moore using a HNU meter to

insure that worker exposure levels were well below OSHA requirements. Once installed, the low manhole served as a sump point and pumping manhole for dewatering operations. The installation of the pipe involved a seven-part process, including installation of the sheeting box, excavation, placement of the impermeable liner and filter fabric, installation of the pipe and filter stone, installation of the drainage core, backfilling and removal of the sheeting box. Upon completion of the interceptor/collector pipe installation, the 2-inch force mains were installed from the pumping manholes to the temporary organic treatment system. Permanent electric pumps were installed in each pumping manhole to pump water to the treatment system. The interceptor/collection trench was then operational.

The temporary treatment system will be terminated once the client has obtained the capability to treat organics in his industrial waste treatment facility. NYSDEC and USEPA required treatment of the organics to less than 10 ppb prior to discharge.

NYSDEC permitted installation of the Disposorb units in a parallel mode only during construction, since the units were new and construction was anticipated to extend about three months, well below the time required for breakthrough. After construction, NYSDEC required placement of two Disposorb units in a series mode to provide redundancy in case of breakthrough. In addition, after completion of construction, NYSDEC required replacement of the three first-series units prior to operation. As a result, the system is capable of handling 30 gpm as shown on Figure 6.

The system is connected to 2-inch diameter force mains extending from the two manholes at the lowest elevations to the bag filters for removal of suspended solids. After removal of the suspended

solids, the ground water passes through the Disposorb units for organic removal. The effluent from the Disposorb units is then discharged to an industrial waste line for inorganic treatment at the industrial waste treatment facility.

PROBLEMS ENCOUNTERED

Originally, construction was anticipated to begin in early summer and the client's industrial waste treatment facility capability to handle organics was anticipated to be on line before winter. However, delays in obtaining the required regulatory approvals as well as delays in completing the organic treatment capability at the client's industrial waste treatment facility necessitated replanning the construction and operation for winter time. As a result, a heated shed, capable of containing the seven Disposorb units required during construction, had to be constructed.

Occasionally, water infiltration, through the corners of the sheeting box and into the excavation, was greater than expected. This was troublesome in areas where sands immediately overlying the clay were particularly silty. The water flowing into the excavation transported silt, so that both dredging of the silt and pumping of the water were necessary prior to any pipe installation. In addition, during construction the high silt content periodically clogged the bag filters, necessitating replacement of the filter bags.

The process of installing the sheeting box, pipe and associated filter fabric and drainage core was initially very time consuming, especially in the deep sections of the alignment. However, once the Contractor delegated specific responsibilities to the crew, efficiency dramatically increased.

RESULTS

Preliminary monitoring of the influent and effluent entering the temporary treatment facility indicates that total VOA's exceeding 300 ppb which enter the Disposorb units are reduced to 1 ppb in the effluent.

During operation, influent and effluent monitoring of each series of GAC units will be performed on a weekly basis to insure that breakthrough does not occur.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

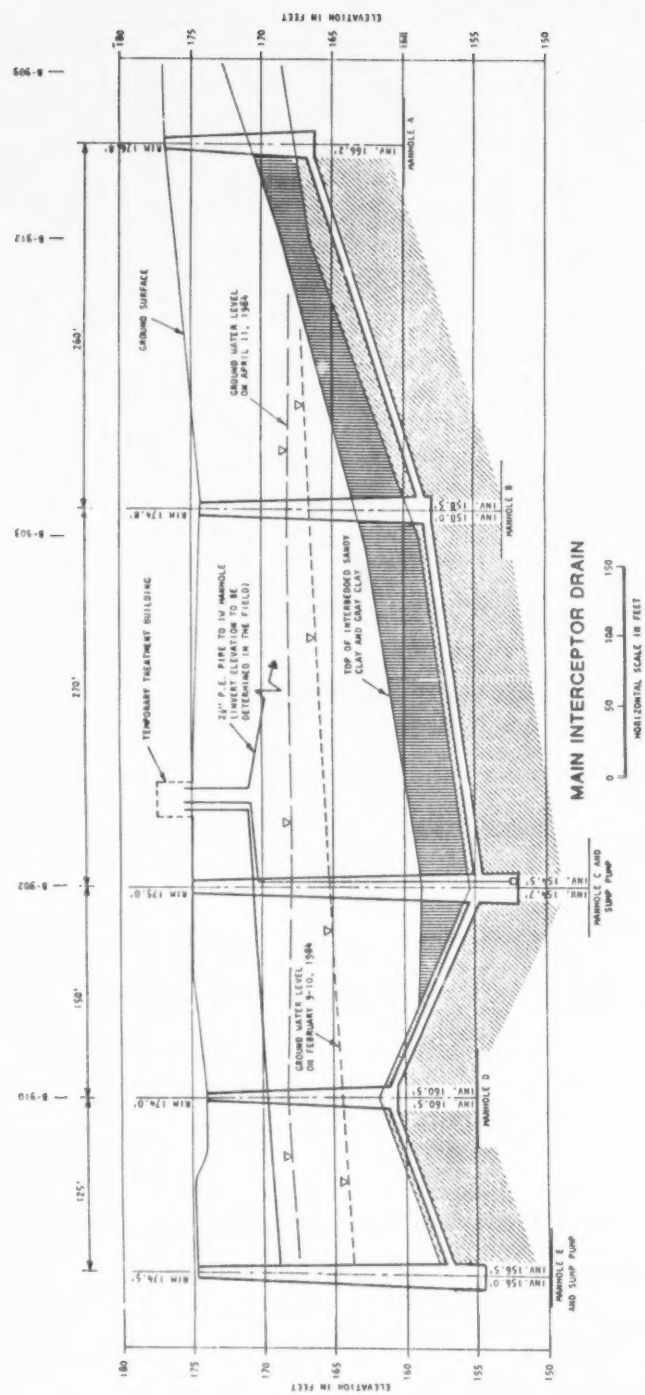


FIGURE 2

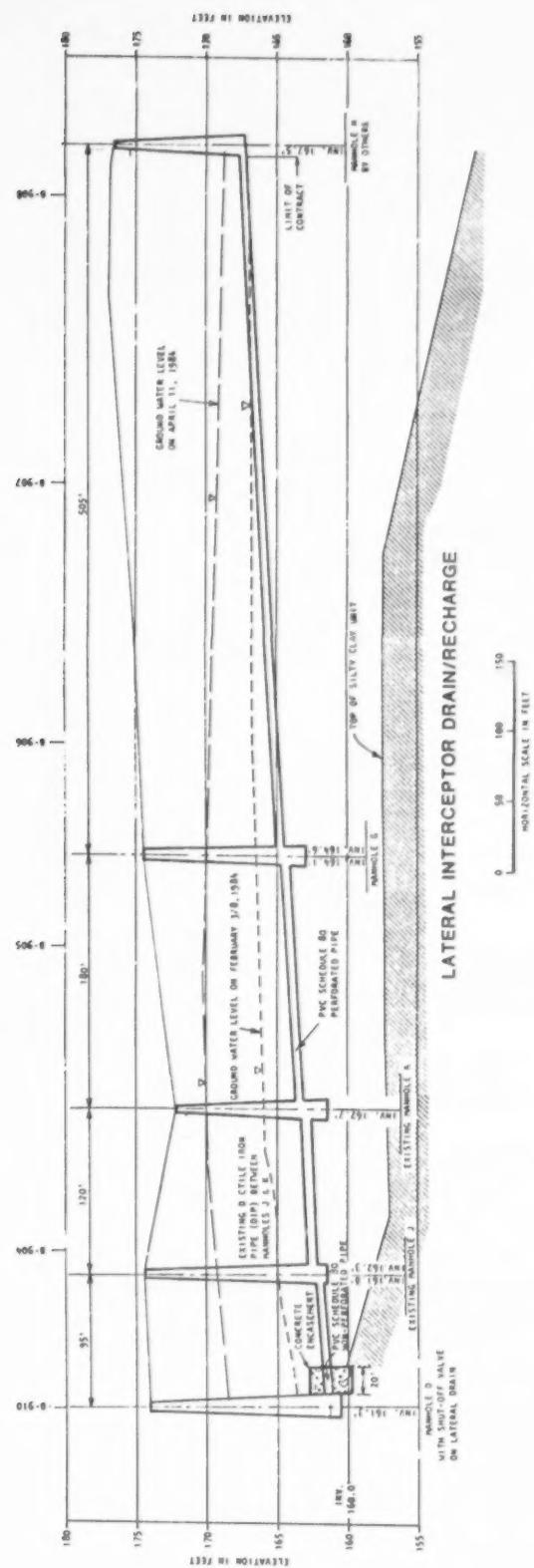
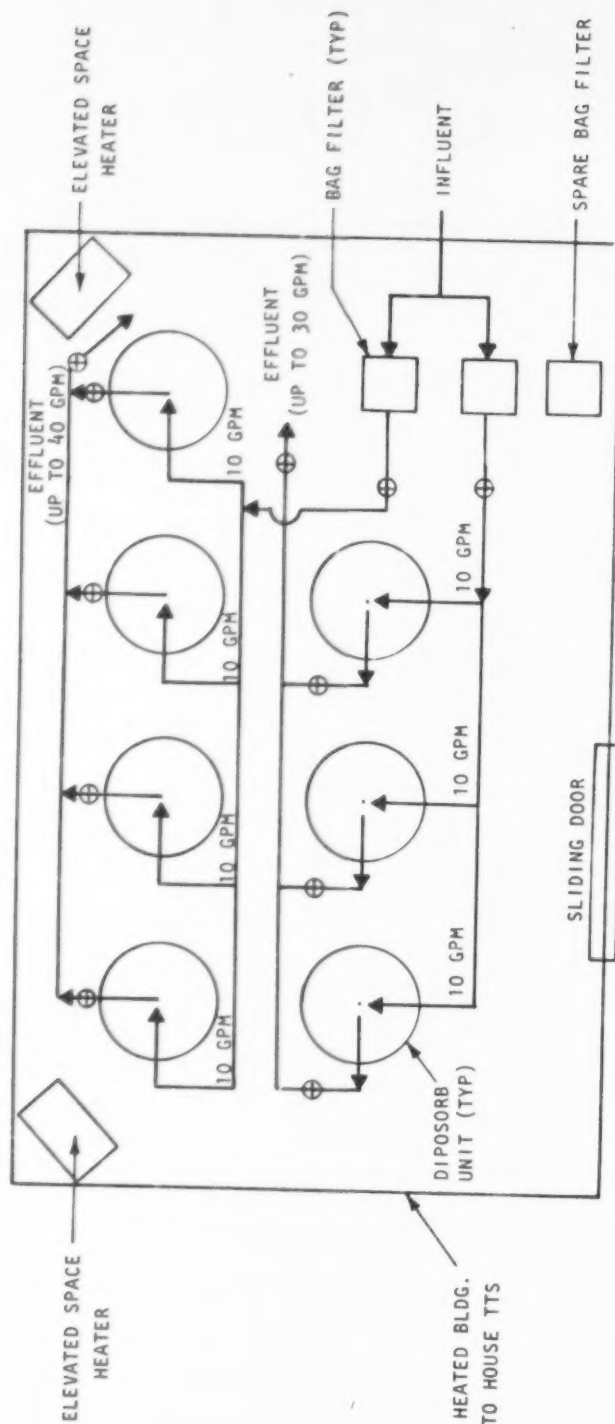


FIGURE 4

CONFIGURATION DURING CONSTRUCTION



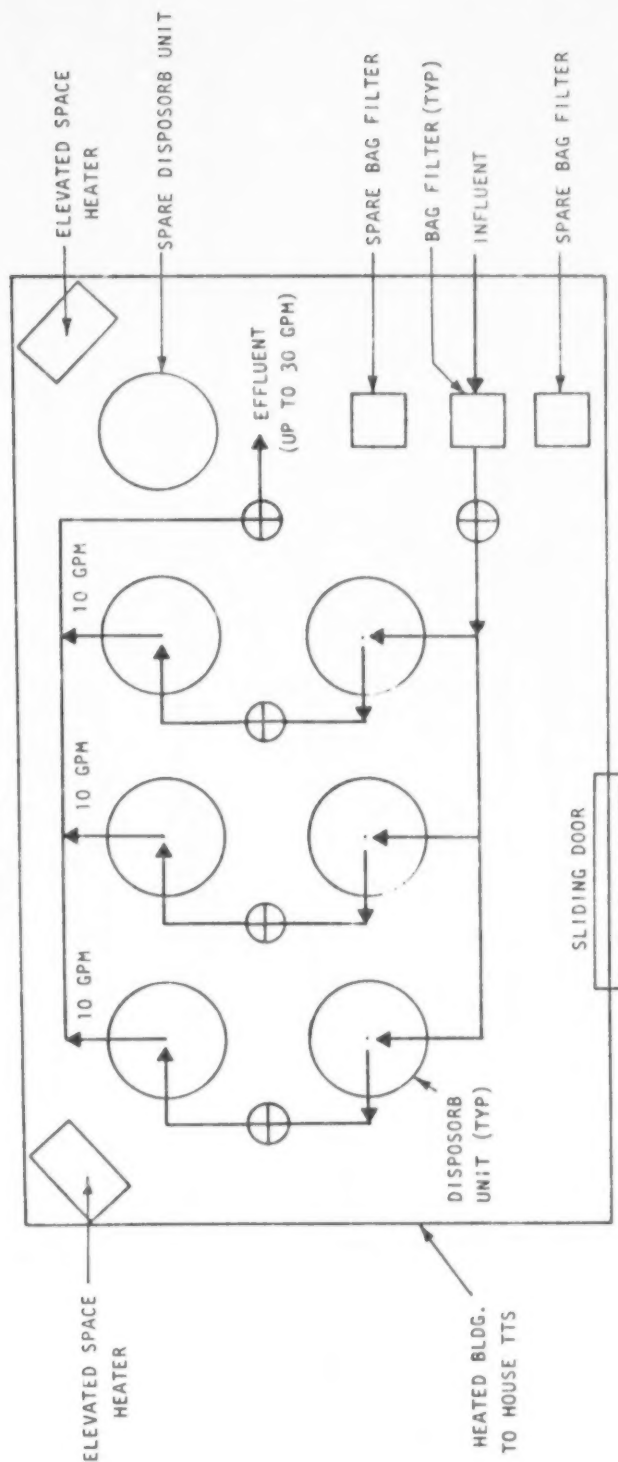
NOTES:

1. 7 CALGON DIPOSORB UNITS (10 GPM TREATMENT CAPACITY EACH) WILL BE CONNECTED IN 2 CLUSTERS OF 3 AND 4 UNITS EACH FOR OPERATION DURING CONSTRUCTION.
2. ROSEDALE OR SIMILAR BAG FILTER WILL BE USED TO REMOVE SUSPENDED SOLIDS TO 0.5 MICRONS.
3. ⊕ DENOTES AVAILABLE SAMPLING POINTS.

TEMPORARY TREATMENT SYSTEM (TTS)

FIGURE 5

CONFIGURATION POST CONSTRUCTION



- NOTES:
1. 6 CALGON DISPOSORB UNITS (10 GPM TREATMENT CAPACITY EACH) WILL BE CONNECTED IN 3 SERIES OF 2 UNITS EACH FOR OPERATION AFTER CONSTRUCTION.
 2. ROSEDALE OR SIMILAR BAG FILTER WILL BE USED TO REMOVE SUSPENDED SOLIDS TO 0.5 MICRONS.
 3. $\oplus$ DENOTES AVAILABLE SAMPLING POINTS.

TEMPORARY TREATMENT SYSTEM (TTS)

FIGURE 6

MICROBIAL DETOXIFICATION OF CYANIDE FROM WASTEWATER

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ABSTRACT

Industrial wastewater containing cyanide must be treated before discharging into the environment as it is toxic to mammalian and aquatic life. Though alkaline chlorination process (chemical) is generally advocated, biological methods - comparatively cheaper, can be tried for cyanide removal. Biodegradation of alkali cyanide in acclimated trickling filter and activated sludge process as well as by pure microbial isolates have been reported in literature. The paper deals with the work carried out in laboratory model continuously fed complete mixing aeration system - seeded with cyanide acclimated microbial sludge, on following aspects - (i) Microbial detoxification of cyanide, (ii) Influence of zinc, copper and cadmium on cyanide biodegradation and (iii) Feasibility studies for cyanide removal in wastewater from a gold ore processing system.

The biological system was operated at a hydraulic detention time of $12\frac{1}{2}$ hr. The experimental results revealed that (i) Cyanide could be degraded effectively at cyanide loading of 0.130 - 0.131 g CN^- /g MLSS/day and the effluent had less than 0.2 mg/l CN^- . Assay of bioreactor MLSS for microbial counts showed that cyanide resistant counts were more or less same with peptone and sewage - 2.8×10^7 /ml and the total viable counts were 7.8×10^7 and 3.0×10^8 /ml respectively, (ii) Zinc at 50 mg/l and cadmium below 20 mg/l did not affect cyanide biodegradation while copper even at 5 mg/l affected cyanide removal, (iii) Cyanide present in the gold ore processing wastewater could be removed to the extent of 79 to 87 percent and (iv) there was significant removal of the metals during the treatment and were found to be associated with MLSS.

INTRODUCTION AND PURPOSE

Treatment of cyanide containing waste waters is an important concern in industries where it is used or produced. This is because cyanide is highly toxic to mammalian and aquatic life. In certain

waste waters like plating mill and gold ore processing, cyanide also occurs as heavy metal complexes. Generally alkaline chlorination is the method of choice for cyanide destruction. However, biological treatment systems which would be comparatively cheaper, have

been investigated by several workers. Biodegradation of simple alkali cyanide in activated sludge process (1-4) and both simple and heavy metal complex cyanide in trickling filters (5-7) have been investigated. It has been found by these investigators that simple cyanide can be degraded by these processes after acclimation. However, though zinc and cadmium cyanide complexes were found to be degraded by acclimated trickling filters, copper and iron complexes were found to be poorly removed (7). Further the extent of influence of heavy metals on cyanide biodegradation in a completely mixed aeration system (CMAS) as well as studies on amenability of cyanide biodegradation in gold ore processing waste water appears to have not been carried out.

The purpose of this investigation was to establish the biodegradation of alkali cyanide by the specific microbial sludge developed in this laboratory in a CMAS and to find the influence of zinc, cadmium and copper on cyanide biodegradation as well as to study the feasibility of biological removal of cyanide from gold ore processing waste water which also contained heavy metals like zinc and copper in significant concentrations.

APPROACH

Bench Model CMAS

Studies were carried out

to find the biodegradation of cyanide by continuous feeding experiments. A bench model CMAS consisting of an aeration unit of two litre working volume with a built-in settling chamber was used for the study. The cyanide containing waste water was placed in a reservoir and fed to the aeration unit by either a solution metering or electrolytic feeding pump. A line diagram of the assemblage is given in Figure 1. Compressed air was supplied for aeration. Microbial sludge was developed in the aeration unit with synthetic cyanide waste containing peptone/domestic sewage as organic nutrients. The unit was also seeded with a cyanide

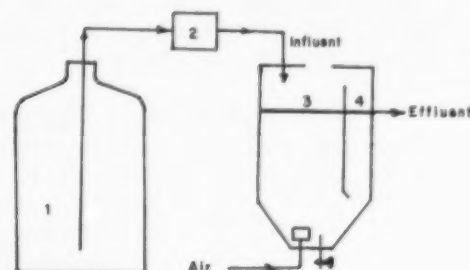


Figure 1. Bench Model diagram of CMAS.

- 1-Feed Reservoir;
- 2-Feeding Pump;
- 3-Aeration Chamber;
- 4-Built-in settling Chamber.

degrading organism *Pseudomonas acidovorans* which was isolated in this laboratory. The system was put to continuous operation after building up the microbial sludge to around 1000 mg/l as mixed liquor suspended solids (MLSS).

Preparation of Waste Water

In all these experiments either peptone (50 mg/l) or settled domestic sewage (1 hr settling) was used as organic nutrients. Water of following composition was used for preparation of synthetic cyanide waste - sodium bicarbonate 250 mg; potassium dihydrogen orthophosphate 50 mg; magnesium sulphate 50 mg; calcium chloride 20 mg; ferric chloride 1 mg and distilled water one litre. Settled sewage was mixed with synthetic cyanide waste in equal proportions (V/V) for the experiments on biodegradation of alkali cyanide. For studies on influence of heavy metals peptone was incorporated in the synthetic cyanide waste. The cyanide concentration was kept more or less constant and the metal's concentrations were varied. The metals were tested individually and added to the synthetic waste as their sulphates after the addition of cyanide so as to avoid their precipitation. In feasibility studies with gold ore processing waste waters the sewage was mixed with the waste water at 1:3 proportion (V/V).

Source of Gold Ore Processing Waste Water

The beneficiation of crushed ore results in the separation of gold and waste rock known as tailings. The gold from fine ore which may not settle in the gravity separation process is taken to cyanidation plant for proper dis-

solution of gold. Sodium cyanide is used as transfer agent. Process waste water is discharged from cyanidation plant, vacuum filter, zinc extraction boxes and from acid vats. The waste water from the processes is collected in the residue tank and pumped to a series of dump pits in the tailing site. The settled waste water from the residue tank (after settling the tailings) was collected for the studies.

Sampling and Analysis

The CMAS was operated at hydraulic detention time of around 12+1 hr. Random samples were collected after the system reached steady state and subjected to analysis. The analytical methods adopted for cyanide, metals, biochemical oxygen demand (BOD), chemical oxygen demand (COD) and MLSS were as per the procedures given in Standard Methods(8). The heavy metals were determined by Atomic absorption spectrophotometer. The microbial assay of the reactor contents for total viable and cyanide resistant counts were carried out as per the procedure given in our earlier paper(4). The pH was determined with pH meter. In tables cyanide and heavy metals are expressed as CN^- and as individual metal respectively.

RESULTS

Biodegradation of Simple Cyanide

The CMAS was operated with

synthetic cyanide waste, first containing peptone and later with sewage. The BOD and COD of the sewage used in this study were 158 and 279 mg/l respectively and they were estimated to only know the organic content of the same. Cyanide in influent and effluent as well as MLSS of the bioreactor (Aeration unit) were estimated. The results are presented in Table 1. The cyanide loading with peptone and sewage were worked out to be 0.131 and 0.130 g CN⁻/g MLSS/day respectively. It could be seen that cyanide could

TABLE 1. BIODEGRADATION OF CYANIDE IN CMAS

Parameter	Peptone	Sewage
No. of obser.	11	6
Cyanide, mg/l		
Influent AM	91.10	115.50
SD	6.92	14.70
Effluent AM	0.02	0.18
SD	N.C.	0.02
% Reduction	99.97	99.84
MLSS, mg/l		
AM	1390.00	1766.00
SD	106.80	318.80
pH		
Influent	9.1-9.4	9.1-9.4
Effluent	8.9-9.0	8.7-8.9

N.B. AM = Arithmetic Mean,
SD = Standard Deviation,
NC = Not Calculated.

be degraded by the microbial flora and there was more than 99 percent reduction. The microbial status of the bioreactor MLSS were assayed and the results are presented

in Table 2. The presence of cyanide resistant counts further confirms the cyanide metabolism in the system and the

TABLE 2. MICROBIAL STATUS OF CMAS.

Parameter	Peptone	Sewage
No. of obser.	6	5
T V C per ml		
Minimum	5.8×10^7	2.4×10^8
Maximum	9.7×10^7	3.8×10^8
A. Mean	7.8×10^7	3.0×10^8
C R C per ml		
Minimum	4.6×10^6	9.0×10^6
Maximum	4.6×10^7	4.6×10^7
A. Mean	2.8×10^7	2.8×10^7

N.B. TVC = Total Viable Count,
CRC = Cyanide Resistant Count.

counts were more or less same in both the experiments (with peptone as well as sewage). The total viable counts were more with sewage as compared to peptone. This could probably be due to the inherent flora of sewage which might have proliferated uninhibited. The microbial status also indicated that there were more satellite organisms present in the system other than cyanide resistant ones as the total viable count was more than the cyanide resistant count.

Influence of Heavy Metals

The most common heavy metals that occur with cyanide in certain wastes are zinc, cadmium, copper and iron. Since complex iron cyanide has

indicating that cyanide biodegradation by the microbial sludge was severely affected by cadmium at this concentration.

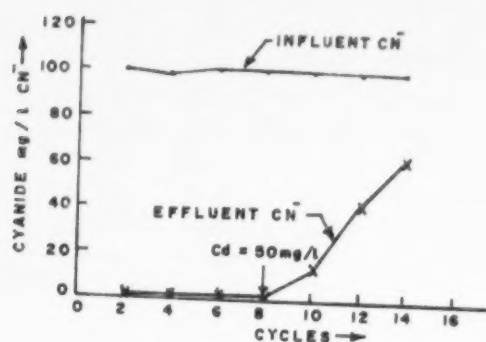


Figure 2. Influence of 50 mg/l Cadmium on cyanide degradation.

The pH of the influent and effluent were also recorded and were in the range of 8.8 to 9.3 and 8.6 to 8.8 respectively. The results of the analysis of the MLSS for the metals at one of the influent concentrations for each metal are given in Table 4.

TABLE 4. DEMONSTRATION OF METALS IN SLUDGE

Metals	Influent (mg/l)	Sludge (mg/g MLSS)
Zinc	25	217.50
Cadmium	5	4.85
Copper	5	1.34

The metals zinc and cadmium are found to be associated more with the MLSS than copper. This is also reflected at the lower concentration of zinc and cadmium in

the effluent and also at poor removal of copper (Table 3). Once the cyanide is degraded, the alkaline pH of the contents could have favoured precipitation of zinc and cadmium and hence they would have appeared in the MLSS. Cheng *et.al* (9) while studying the effect of pH on the removal of heavy metals in the activated sludge process, have reported that considerable precipitation of metal hydroxides could take place at high pH.

Studies with Gold Ore Processing Waste

The waste water was collected twice from the site. The characteristics of the waste are given in Table 5. The cyanide was 24 and 34 mg/l and the waste also showed the presence of copper and zinc in significant concentrations. Presence of zinc in the waste was due to its use in gold extraction process. The higher value of zinc in sample 2 was due to a discharge from acid vat at that time of collection. Sample 1 and 2 were used for peptone and sewage supplementation studies respectively. The BOD and COD of

TABLE 5. CHARACTERISTICS OF THE WASTE WATER

Parameter	Sample 1	Sample 2
Cyanide, mg/l	24.00	34.00
C.O.D., mg/l	286.00	438.00
Zinc, mg/l	7.85	46.00
Copper, mg/l	8.39	12.90
Iron, mg/l	0.38	0.45
pH	7.20	7.50

TABLE 3. INFLUENCE OF HEAVY METALS ON CYANIDE BIODEGRADATION

Metal (No. of observations)	Metal Infl	Conc. mg/l		Cyanide as CN, mg/l		MLSS mg/l
		Effluent	Mean(S.D.)	Influent	Effluent	
				Mean(S.D.)	Mean(S.D.)	Mean(S.D.)
Zinc	(8) 10	0.07(N.C.)		98.6(6.63)	0.20(0.01)	1080(70.4)
	(8) 25	0.04(N.C.)		97.4(2.67)	0.18(0.01)	1370(173.4)
	(8) 50	0.12(0.19)		98.2(6.96)	0.19(0.02)	2175(336.0)
Cadmium	(9) 5	0.13(0.02)		95.6(3.50)	0.17(0.02)	1645(148.8)
	(5) 10	0.60(0.50)		97.4(7.00)	0.18(0.02)	1490(41.8)
	(5) 20	0.56(0.09)		100.0(0.76)	0.18(0.01)	1430(41.8)
Copper	(7) 5	4.06(1.28)		96.7(2.45)	2.00(0.40)	1064(55.6)
	(6) 10	8.50(0.56)		96.1(2.00)	16.20(3.60)	1025(68.9)
	(6) 20	17.60(1.00)		97.0(1.00)	28.50(2.00)	825(68.9)

N.B. SD = Standard Deviation; NC = Not Calculated

been reported to be more refractory to biodegradation(7) the studies were restricted to zinc, cadmium and copper. The concentrations tested were upto 50 mg/l in the case of zinc and cadmium, and 20 mg/l in case of copper. The concentration intervals were, however, selected arbitrarily. A known concentration of the metals (pre-estimated in the stock solution) were added to the synthetic waste and hence the influent was not analysed for the metals. The cyanide in the influent and effluent, the metals in the effluent and the MLSS of the bioreactor were estimated. The results are presented in Table 3. It could be seen that zinc upto 50 mg/l and cadmium upto 20 mg/l did not influence cyanide removal and the effluent showed less than 0.2 mg/l. However, copper even at 5 mg/l showed comparatively less removal of cyanide and its removal deteriorated with increasing copper

concentration. Pettet and Mills(7) also found that the acclimated biofilter was not able to effectively remove cyanide from the waste containing alkali copper cyanide complex. However, they found effective cyanide removal when fed with zinc and cadmium alkali cyanide waste. They attributed the ineffective removal of cyanide in presence of copper as due to more stable complex copper would be forming with cyanide.

The results of effect of cadmium at 50 mg/l is given in Figure 2. The cyanide in the influent and effluent are shown in it. The CMAS was working at 20 mg/l of cadmium in the influent initially. At the point indicated in the figure with an arrow, Cadmium in the influent was raised to 50 mg/l. One cycle shown in the figure is equivalent to two litres of waste fed in 12 hrs. It could be seen that at 50 mg/l, the effluent quality with respect to cyanide deteriorated

the sewage -- 74 and 270 mg/l respectively, were determined only to know the organic load of the same.

Cyanide and the metals in the influent and effluent as well as MLSS in the bioreactor were estimated. The results are presented in Table 6. The average MLSS in the bioreactor with peptone and sewage were 960 (SD =153) and 2168 (SD= 503) mg/l respectively.

TABLE 6. PERCENTAGE REDUCTION OF CYANIDE & METALS

Parameter	Peptone	Sewage
Cyanide,mg/l		
Influent AM	21.50	21.20
SD	0.86	4.20
Effluent AM	2.80	4.40
SD	1.28	1.87
%Reduction	87.00	79.24
Zinc, mg/l		
Influent AM	7.60	31.00
SD	0.13	15.16
Effluent AM	2.20	4.08
SD	0.66	5.69
%Reduction	71.05	86.84
Copper,mg/l		
Influent AM	7.04	9.48
SD	0.61	0.76
Effluent AM	3.93	3.37
SD	1.53	1.94
%Reduction	44.18	64.45
Iron, mg/l		
Influent AM	0.43	0.43
SD	0.08	0.06
Effluent AM	0.37	0.28
SD	0.07	0.11
%Reduction	13.95	34.88
pH		
Influent	7.1-7.2	7.4-7.5
Effluent	7.6-7.8	8.4-8.6

N.B. The values are Arithmetic Mean (AM) of 7 observations.

SD = Standard Deviation.

The results obtained showed that the cyanide in the waste water was amenable for biodegradation. However, the removal of cyanide was not to the extent that was obtained with simple alkali cyanide (Table 1) or with zinc alkali cyanide complex (Table 3). This could be due to the presence of copper (ineffective removal of cyanide in presence of copper -Table 3) as well as iron.

The mixed liquor suspended solids were also assayed for the metals on three occasions during each experiment. The results showed that zinc, copper and iron were found to be with the solids and were in the range of 35.2 to 107.1, 2.4 to 22.2 and 1.1 to 4.5 mg/g suspended solids respectively. The zinc content was found to be more as compared to other metals.

From these studies following conclusion can be made -
 (i) Biodegradation of simple alkali cyanide could be effectively brought about in the biological system with the acclimated microbial sludge,
 (ii) Zinc upto 50 mg/l and cadmium upto 20 mg/l did not influence cyanide biodegradation. However, copper even at 5 mg/l affected effective removal of cyanide, (iii) Though cyanide present in the gold ore processing waste could be biologically degraded to a sig-

nificant level (79.24 to 87.0 percent reduction), its removal to the extent desired (less than 0.2 mg/l) was not obtained. This limitation has to be taken into account before suggesting a biological treatment system for gold ore processing waste water and (iv) During the treatment of waste waters, the metals were found to be associated with the MLSS. Their continuous emergence in the bioreactor can also result in the retardation of microbial activity on a long term basis.

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REVIEW OF CURRENT PRACTICES FOR REMOVAL AND DISPOSAL OF ARSENIC AND ITS COMPOUNDS IN JAPAN

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ABSTRACT

Wastes containing arsenic are generated not only during production of arsenic and its compounds, but also from production of non-ferrous metals, non-metals (phosphorus, fertilizers, etc.), geothermal power generation, electronic industry processes, and large-scale applications of pesticides and wood preservatives. Liquid and gaseous waste streams containing arsenic, due to their hazardous nature, must be treated before they are released into the environment.

A flowsheet briefly summarizing qualities and uses of arsenic and its compounds in Japan is presented. At the present time there are no visible undesirable effects of the treatment and disposal methods currently practiced in Japan. Some specific treatment and disposal methods are described.

INTRODUCTION

Arsenic and arsenic compounds are used for many different applications such as: insecticides, herbicides, dessicants, rodent control, and animal food additives. When swallowed, all of them cause acute poisoning; chronic poisoning could also result from inhalation (1). Besides their toxic nature, arsenic and its compounds are also explosive and ignitable, and therefore they are classified as hazardous materials. The wastes obtained from production of arsenic and its compounds, from mining operations, from production of non-ferrous metals, non-metals (phosphorus, fertilizers etc.), from electronic industry sources, from sludge treatment, and from combustion (2) are treated as hazardous metals.

Flow of Arsenic (Figure 1).
Until recently a large amount of arsenic (as As_2O_3) was imported to

Japan from France, the USSR, and the People's Republic of China. Arsenic coming from China was rather of low quality, but inexpensive (approximately ¥200/kg). During 1984 no arsenic was imported to Japan. Most of the arsenic currently comes from copper refineries in the form of As_2S_3 , which is converted to As_2O_3 . There are three major companies which handle nearly 100 percent of arsenic production - Furukawa, Sumitomo and Onahama. Annual production of As_2O_3 is approximately 865 tons/year. From this quantity approximately 200 tons/year of high quality product (approximately ¥400-500/kg) are exported to South-East Asia, Australia and America. Distribution of the remaining production is as follows: 300t/y is used for production of pesticides, wood-treatment agents, animal food additives, etc.; 200 is used in zinc refineries; 150 is used in glass production; 15 is used for production of arsenic in metal form used in semiconductor industry. The above numbers represent only the approximate distribution of the As_2O_3 among

different industries. About 1 of arsine (AsH_3) is imported from the United States for production of semiconductors. Part of the zinc refineries' wastes containing high concentrations of arsenic are returned to the manufacturers (3).

The manufacturers of As_2O_3 , as well as the other users of the product, use conventional chemical precipitation, coagulation, and sedimentation processes to obtain sludges which are taken to land disposal or used for reclaiming land from Tokyo Bay. The semiconductor industry also uses a special adsorption process (TOXO-CLEAN) and these wastes are stored in old mines. Another source of arsenic is geothermal power generation. Most of this arsenic is removed by precipitation-sedimentation treatment, while some small quantities in low concentrations are released directly into the environment. Pesticides and wood-decay prevention agents are directly released into the environment. Land disposal also contributes to the direct environmental discharge.

TREATMENT

Most treatment processes include chemical precipitation and separation of solids by sedimentation. Obtained sludges are sometimes further treated for safe final disposal. A few of the current practices, including some details, will be presented here.

Treatment of water in a geothermal power generation plant. The processes presented here are employed by Kyushu Electric Company at their Ohdake, Hachiohahara Plant in Ohita Prefecture, Kyushu (4). The water and steam from a geothermal well enter a separator. Steam goes to turbines while the separated water enters a holding tank. A portion of the water is returned to the underground well,

while the rest of the water is pumped into a reactor where $150 \text{ m}^3/\text{hr}$. of water are treated. The water entering the reactor has approximately 2-3 ppm of arsenic with a pH of 7.5-8.5. This water is mixed with 3.9 ℓ/h of 70% sulfuric acid (H_2SO_4), 14.9 ℓ/hr of NaOCl (containing 7% Cl_2) and 10 ℓ/hr of FeCl_2 solution (containing 13% of Fe). The pH value in the reactor is between 3 and 4. The reactor effluent enters a mixing tank where NaOH (22%) solution is added and the pH is raised to between 4 and 4.5. The slurry from the mixing tank goes into a filter press. The solids are taken by conveyor belts into storage, from where they are transported to final disposal sites. Production of solids is approximately $1.5 \text{ m}^3/\text{day}$. Depending on the concentration of arsenic, the filtrate may be stored in the liquid waste storage tank and recycled to the head of the treatment processes, or treated with NaOH solution (22%) so that the pH value is raised to 5.8-8.6. Arsenic concentration in the treated water is below 0.05 ppm, and this water is directly released to the environment. Cost for this treatment is approximately $\text{\$}150/\text{m}^3$ (approximate U.S. $\text{\$}0.60$).

The chemistry of this process basically is given by the following equations:



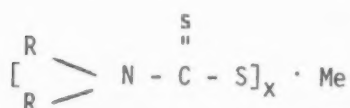
Ferric arsenate is little soluble in pH range of 5-8. The schematic flow chart of the process is presented in Figure 2.

Treatment of wastewater containing arsenic and gallium from semi-conductor production. Nippon Electric Company (NEC) has developed a process for removing arsenic and recovering expensive gallium from wastewater in a Ga-As semiconductor production plant (5). The process involves coprecipitation of arsenic and gallium by $\text{Fe}(\text{OH})_3$ (addition of FeCl_3 and NH_4OH) at

pH values below 7. The precipitate, separated from the supernatant by filtration, is suspended in water and NaOH is added to raise pH above 9 (usually to approximately 13) to redissolve galium. The arsenic remains in solid form and is removed by filtration. The removal of arsenic is above 95%. The separated sludge containing arsenic, is taken to a solid waste disposal site.

For example, to a wastewater containing 10 ppm As and 10 ppm Ga, 100 ppm of Fe(III) was added and mixed with aqueous NH_4OH to raise the pH to 5.2. The coprecipitate, after separation, was suspended in water and mixed with NaOH to raise the pH to 13. Arsenic concentration remaining in the solution containing galium was below 0.5 ppm.

Treatment of wastewater containing arsenic from cadmium refining. Nippon Mining Corporation has a patent for removal of arsenic from low pH wastewaters (6). The process is most efficient when the pH is between 1 and 2.5, and it is recommended only for pH below 3. The treatment utilizes dialkyl thiocarbamate as a chelating agent. The alkyl group (R) can be methyl, ethyl or n-bentyl. The compound makes metal (Me) complexes of the following form:



which are precipitated. For removal of arsenic from cadmium refining wastes R_2NCSSNa was used. The usual ratio of dialkyl thiocarbamate to arsenic ranges from 1 to 5. The wastewater was mixed with approximately 1 equivalent of dialkyl thiocarbamate at 400 RPM for 30 minutes at different pH values. Best results are achieved with dimethyl carbamate at approximate pH value of 1.1. More than 95% of

arsenic is removed. The precipitate is incinerated and arsenic is recovered. There are no disposal problems related to this process.

Removal of arsenic from wastewater by use of synthetic resins. Unitika Ltd., a large manufacturer of synthetic fibers, has a patent for removal of arsenic from wastewaters having low concentrations of arsenic (like geothermal waters with 2-3 mg/L) (7). A chelating resin containing $\text{CH}_2\text{N}=\text{R}$ $\text{CH}_2[\text{CH}(\text{OH})]_n \text{CH}_2\text{OH}$ moiety, where R is H or C_{1-5} alkyl and n is 1 to 6, is used. The adsorption capacity for Amberlite IRA 743 was 30 mg As^{3+} /mL of resin.

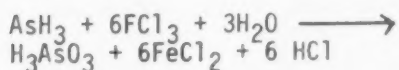
Treatment of arsenic containing wastewaters with titanium compounds. Mitsubishi Rayon has developed a process for removal of arsenic from wastewaters that contain several metal ions (8). The process is used by the electronic industry. Wastewaters containing arsenic are treated with a titanium compound $(\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4)$ to form titanate acid, which forms a coprecipitate with arsenic. In a wastewater initially containing 97mg/L of arsenic, the concentration after coprecipitation and filtration was reduced to 0.026-0.054 mg/L. The process is most effective in the pH range between 2 and 8. The only disadvantage is that the process is rather lengthy - 16 hours. Other titanium compounds could be used, like TiCl_4 or TiOSO_4 .

Adsorption of arsenic by red mud. A very low cost process for removal of arsenic was developed by the Agency of Industrial Sciences and Technology (9). Red mud, obtained from aluminum production, usually contains approximately 17-25% of Al_2O_3 , 25-50% of Fe_2O_3 and 5-20% of SiO_2 . Al_2O_3 and Fe_2O_3 adsorb arsenic. In the pH range between 5 and 7 removal efficiency is over 99%. Wastewater containing arsenic is shaken with red mud for 24 hours. The red mud could be shaken in 0.01 N sodium hydroxide for 24 hours, separated and reused. The main advantage

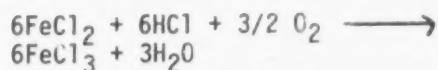
of the process is its low cost.

Treatment of waste gases containing Arsine. Toyo Oxygen Co., Ltd. manufactures a system (TOXOCLEAN SYSTEM) that reduces the concentration of arsenic in waste gases, generated by the semiconductor production processes, to meet emission standards (10). A schematic sketch of the process is presented in Figure 3. The exhaust gases pass through a combustion chamber, Venturi scrubber, bag filter, blower, humidifier and the "TOXOCLEAN". The waste gas enters the combustion chamber through a nozzle which is protected from plugging and backfire with an inert gas curtain. The waste gas is mixed with air in the combustion chamber and the continuous burnings occurs spontaneously. The fine particles formed by combustion are carried with the gas stream into a Venturi scrubber where most of them, as well as acidic compounds, are removed. At the same time the exhaust gas is quenched. The remaining submicron-sized particles are collected by the bag filter. The gas is moved by the blower through the humidifier to control its moisture and temperature. The residual low-level toxic compounds (arsine) are absorbed by TOXOCLEAN. The main ingredient of TOXOCLEAN is FeCl_3 . Auxiliary agents are metal chlorides and metal oxides. Principal processes explaining use of TOXOCLEAN can be written by the following reactions:

Absorption



Reactivation



The absorbing capacity of TOXOCLEAN varies slightly as a

function of flow rate, charging pressure and the amount of available water. On average 1 kg of TOXOCLEAN absorbs about 50 liters of AsH_3 . The effluent stream from the process contains less than 0.05 ppm of AsH_3 .

DISPOSAL

As shown in Figure 1, most of the arsenic containing sludges are land disposed. Since most of these wastes contain insoluble arsenic compounds, they are often disposed in municipal landfills (not hazardous waste disposal sites). There exist several processes that can be used to stabilize sludges containing arsenic so that no leaching will occur.

Sludge can be treated with a 5% aqueous solution of thiourea, sand, and portland cement at pH a of 12.5. Leaching tests show that the leaching from the concrete was far below the regulation levels (11).

Also, a lime neutralized sulfuric acid waste is mixed with lime to pH 12-13, and the heated above 720° to stabilize the heavy metals and arsenic. Arsenic leaching was nil (12).

Currently, arsenic disposal in Japan does not cause any environmental or health problems.

ACKNOWLEDGMENTS

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Figure 1. Arsenic flow in Japan

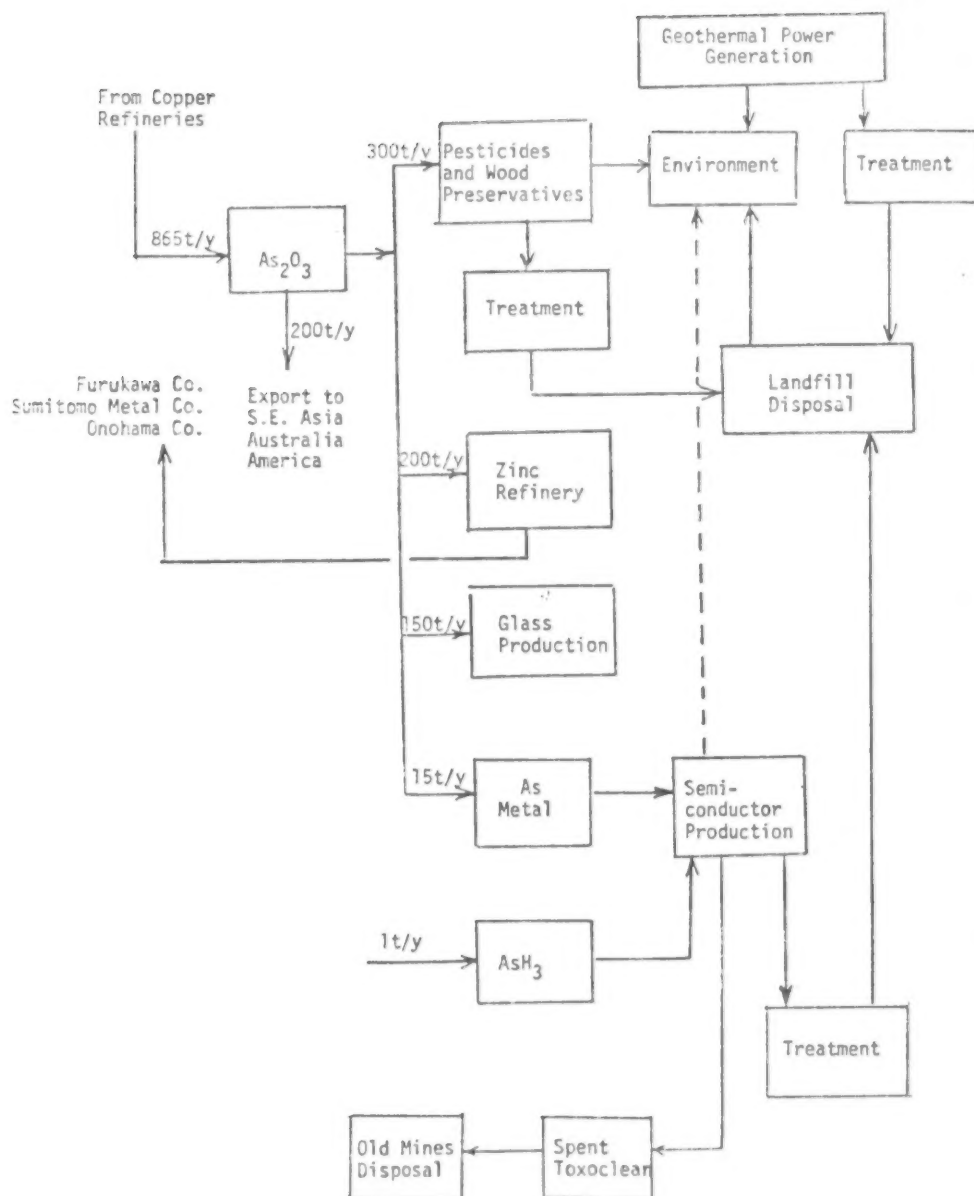


Figure 2. Wastewater treatment in a geothermal power plant

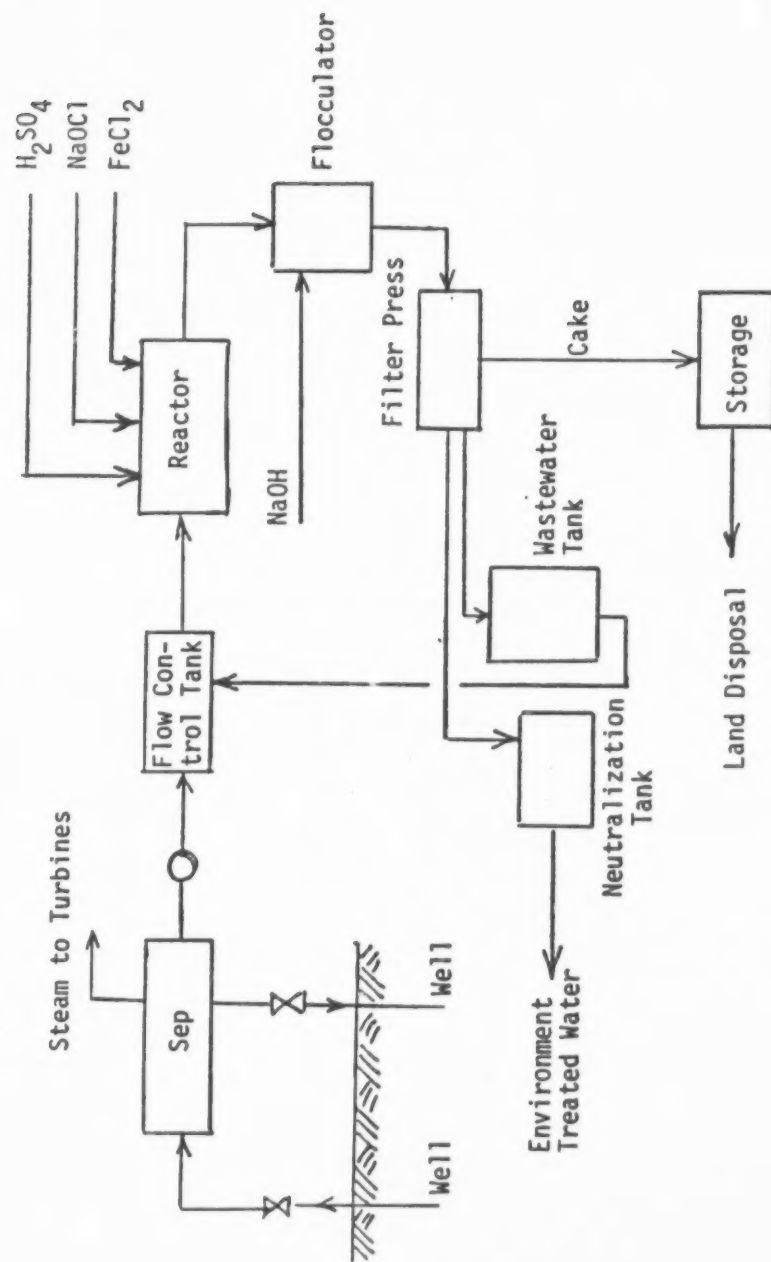
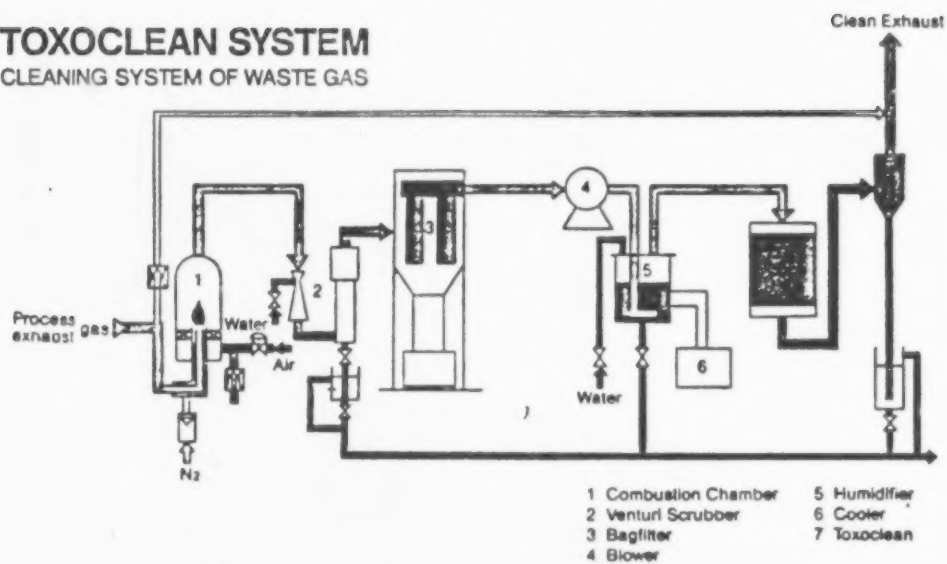


Figure 3.

TOXOCLEAN SYSTEM
CLEANING SYSTEM OF WASTE GAS



A DECISION MODEL RESULTING FROM THE CLASSIFICATION OF HAZARDOUS WASTE

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ABSTRACT

In the global waste flow of each industrialized country, we can measure a specific amount of waste which are hazardous or even toxic. Hazardous waste can be considered from different points of view. The first one leading to a well organized waste management should be a proper systematics and classification of such kind of waste. Before formulating their own new classification of hazardous waste in Poland, the authors analysed 19 known classifications from different countries which included 22 various classification criteria. Toxicity in relation to humans, animals, and plants, was mentioned there 18 times, flammability, 13 times, explosiveness, 8 times, reactivity and water-solubility, 7 times each, etc.

In Poland, in the management of hazardous waste, various classifications are used. Recently, the authors have worked out a modern and new one combining many elements which have proved useful in other classification systems.

The system in question has been divided into a five-rank classification (highly active and toxic substances - class I, hazardous substances, harmful substances, partly noxious substances, and harmless but troublesome substances - class V), and the adopted indicators are as follows: toxicity, flammability and explosiveness, consistence, water-solubility, composition of water extract, volatility, reactivity, and corrosivity. For each class threshold values of particular indicators related to the Polish Poison Act, the Polish Water Pollution Control Act, and to the Polish Clean Air Act have been established. In accordance to the new classification and resulting implications, the authors elaborated a Decision Model based on local and regional solutions.

INTRODUCTION AND PURPOSE

Every waste material may be evaluated in terms of many different criteria. These should be formulated clearly and unequivocally so as to enable a reliable characterization not only of the waste as a whole, but also of its individual properties. Having such data at hand, one is able to take a relevant decision as to whether a given waste

material might be utilized or disposed of.

Of prime importance is that the following groups of criteria be involved, when characterizing the properties of the waste material:

1. those of the recovery of valuable resources included in the waste;

2. those of the technological potential, viz. appropriate methods of processing or disposal, and
3. those of the noxiousness to man and environment, viz. relevant approach to the problem of processing or disposal, and adequate environmental safeguards.

Since noxiousness estimates are of prime significance to decision-making in the management of solid wastes (storage, transport, processing, reuse and disposal), they will be the dominant topic to be considered in this paper.

The classification of waste materials in terms of their noxiousness which is now being in force in Poland has a provisional character (4). Furthermore, it proved to be inadequate to meet the demands made on such classifications. Hence, there is an urgent need to develop a novel classification and set a relevant list of hazardous wastes, providing their detailed characteristics evaluated from three aspects - that of their noxiousness, that of the technological potential and that of the recovery of valuable resources. To this purpose, the authors will make use of literature data, as well as of their own results and experience.

APPROACH

To choose suitable criteria - as well as to select those applied most frequently for the purpose of interest - analyses were carried out on home-developed and foreign classifications of solid wastes in general and hazardous wastes in particular (1,2). Thus, for the twenty-two criteria (which have been made use of in nineteen classifications) the frequency of occurrence is as follows: toxicity to humans, animals and plants, 18 times; flammability, 13 times; explosiveness, 8 times; reactiv-

ity, 7 times; water-solubility, 7 times; volatility, 6 times; aggressive action and irritating action, 6 times; consistence, 4 times, and corrosivity, 4 times.

The account given above may be supplemented by a number of new data obtained by the authors of this paper from their study on the composition and properties of, as well as from the noxiousness estimates for, solid waste generated by various industrial branches.

Finally, eight indicators (criteria) have been adopted for classifying the noxiousness of wastes. These rank as follows:

- A. TOXICITY,
- B. FLAMMABILITY, EXPLOSIVENESS,
- C. CONSISTENCE,
- D. WATER-SOLUBILITY,
- E. COMPOSITION OF WATER EXTRACT,
- F. VOLATILITY,
- G. REACTIVITY, and
- H. CORROSIVITY.

On estimating any of the eight indicators, we make use of a five-rank classification involving the following classes:

- Class I toxic waste,
- Class II hazardous waste,
- Class III harmful waste,
- Class IV partly noxious waste,
- Class V harmless waste.

Each class have been assigned respective threshold values for every component included. These are explicit numerical values complying with Polish rules and regulations which are in force now, viz. the maximum permissible concentration (MPC) values determined for substances creating health hazards in workrooms, the MPC values for airborne substances and pollutants of natural waters, standards for classifying fire and explosion hazards in buildings, corrosive action to building structures, etc.

Thus, taking into account the estimates of individual criteria (of which the following three - toxicity (A), flammability, explosiveness (B) and reactivity (G) - are regarded to be of prime significance), each waste material can be assigned to one of the five classes listed above.

PROBLEMS ENCOUNTERED

The classification presented in this paper must be verified by a continuous investigation of new or insufficiently recognized wastes. Our current knowledge of waste materials, their processing, reuse and disposal is still far from being satisfactory. This simple truth holds for many industrial countries. Continuous advances in industrial technologies make the formulation of adequate criteria (i.e. those for estimating whether or not the given waste is fit for processing, recycling or disposal) lag far behind. The result is that the decision-makers seem to have difficulty in making appropriate use of the available estimation criteria for technological reasons only. And that is why there appeared an urgent need to formulate such criteria for a number of processes (biological stabilization, both aerobic and anaerobic, thermal decomposition, solidification) even at the present state-of-the-art. It often happens that no numerical values are determined. Nevertheless, this situation made it possible to set the course for a further study.

RESULTS

The results obtained from our study enabled a decision model to be formulated for the needs of solid waste management (Fig.1). The determination of such indicators of the wastes as the physico-chemical composition, the class of noxiousness to the environment, recycling potential or technological potential, makes the choice of managerial decisions

more efficient and relevant. Decisions of prime importance should involve the choice of an appropriate method, an appropriate site and an appropriate technological solution when the waste material is fit for recycling and reuse (out of hand or in future). When the waste material is unfit for being recycled or reused, we have to take a decision as to how to solve the problem of storage (type of containers), transport (means of transportation, reloading), primary processing (processes and equipment), processing and disposal. The decision-maker should take into account the regulations for each class of noxiousness included in the classification. Consideration should also be given to technological criteria.

Further decisions should refer to the scale (local or regional) on which the given waste management problem is to be solved. For this purpose, the following parameters are considered: the quantity of the wastes produced, the technological potential, the degree of disposal desired, and the cost of the system involved. A further step in decision-making consists of selecting an appropriate site and an appropriate capacity for the plants where the wastes will be subject to pre-treatment, processing and final disposal. This step must involve environmental, spatial and economic considerations (3).

Successive steps of decision-making in a joint management of solid wastes are included in the decision model (Fig.1). The model also gives successive stages for the identification and classification of the waste. Furthermore, it enables an appropriate choice of methods and procedures so as to meet the requirements of environmental safety.

The model proposed has the merit of being applicable to every kind of

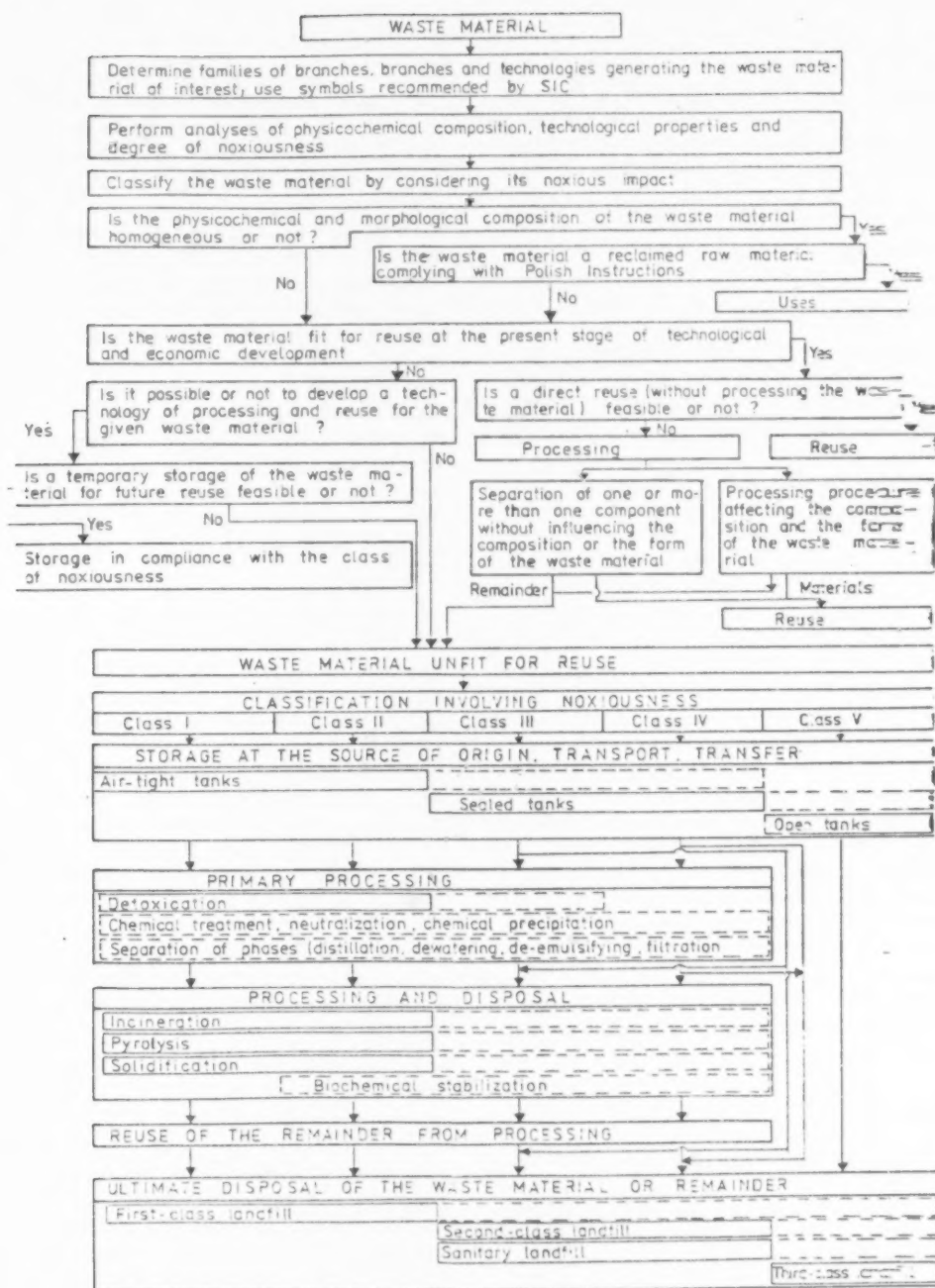


Fig.1 Model of decisions for the needs of hazardous waste management

waste material fit for recycling or disposal, to every source of generation (industrial enterprises) and every region for which rationalized solutions are being planned.

ACKNOWLEDGMENTS

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APPENDIX

Classification of hazardous wastes in Poland

Indicators in details

TOXICITY

Class I - wastes containing, in quantities exceeding 0.1 per cent of dry mass, the following substances:

- a/ those mentioned as poisons - list A in the Polish Poison Act of December 28, 1963,
- b/ those whose MPC in the air of work-rooms does not exceed 0.0001 g/m^3 ,
- c/ those whose MPC (20 or 30 min) in the air in protected areas does not exceed 0.01 mg/m^3 ,
- d/ those whose MPC in surface waters of the first purity class does not exceed 0.05 g/m^3 ,
- e/ those, not mentioned above, whose LD_{50} does not exceed 50 mg/kg (for rats per os) or whose LC_{50} does not exceed 100 mg/kg and other substances of toxic properties corresponding to the above mentioned substances.

Class II - wastes containing in quantities smaller than 0.1 per cent of dry mass the substances of class I and in quantities exceeding 0.1 per cent of dry mass the following substances:

- a/ those mentioned as harmful means - list B in the Polish Poison Act mentioned above,
- b/ those whose MPC in the air of work-rooms varies from 0.0001 to 0.01 g/m^3 ,
- c/ those whose MPC (20 or 30 min) in the air in protected areas varies from 0.01 to 0.1 mg/m^3 ,
- d/ those whose MPC in surface waters of the first class purity varies from 0.05 to 1.0 g/m^3 ,
- e/ those, not mentioned above, whose LD_{50} equals $50-500 \text{ mg/kg}$ or $\text{LC}_{50} = 100-1000 \text{ mg/kg}$ and other substances of toxic properties corresponding to the above mentioned substances.

Class III - wastes containing in quantities exceeding 0.1 per cent of dry mass the following substances:

- a/ those whose MPC in the air of work-rooms varies from 0.01 to 0.1 g/m^3 ,
- b/ those whose MPC (20 or 30 min) in the air in protected areas varies from 0.1 to 1.0 mg/m^3 ,

- c/ those whose MPC in surface waters of the first purity class varies from 1.0 to 10.0 g/m³,
- d/ those, not mentioned above, whose LD₅₀ equals 500-5000 mg/kg and other substances of harmful properties corresponding to the above mentioned substances.

Class IV - wastes containing in quantities smaller than 0.1 per cent of dry mass the substances of class III and in quantities exceeding 0.1 per cent of dry mass the following substances:

- a/ those whose MPC in workrooms exceeds 0.1 g/m³,
- b/ those whose MPC (20 or 30 min) in the air in protected areas exceeds 1.0 mg/m³,
- c/ those whose MPC in surface waters of the first purity class exceeds 10 g/m³,
- d/ those, not mentioned above, whose LD₅₀ equals 5000-15000 mg/kg and other substances of harmful properties corresponding to the above mentioned substances.

Class V - wastes containing no harmful substances LD₅₀ > 15000 mg/kg.

FLAMMABILITY AND EXPLOSIVENESS

Class I - extremely easily flammable and/or explosive wastes:

- a/ wastes evolving gases of lower explosive limit at concentrations up to 10 per cent of volume in a mixture with air,
- b/ wastes containing liquids of an ignition temperature ≤ 294 K. At a given concentration, the vapour of those liquids are ready to form an explosive mixture with air,
- c/ wastes containing solid substances which are flammable when exposed to water or air humidity, or when getting in touch with atmospheric air.

Class II - easily flammable and/or explosive wastes:

- a/ wastes evolving gases of lower explosive limit at concentrations higher than 10 per cent of volume in a mixture with air,
- b/ wastes containing liquids of an ignition temperature between 294 and 328 K; at a given concentration, the vapours of those liquids are ready to form an explosive mixture with air,
- c/ wastes containing fine solids which are ready to form flammable suspensions of fibres and dust particles produced during processing or transport; these occur in amounts facilitating generation of an explosive mixture when getting in touch with atmospheric air.

Class III - flammable and/or explosive wastes:

- a/ wastes containing liquids of an ignition temperature between 328 and 373 K; at a given concentration, the vapours of those liquids are ready to form an explosive mixture with air,
- b/ wastes containing easily flammable solids which occur in amounts insufficient to form an explosive mixture with air.

Class IV - flammable wastes:

- a/ wastes containing liquids of an ignition temperature > 373 K,
- b/ wastes containing either slow-burning solids or such that occur in a form resistant to ignition (e.g. in humid form).

Class V - non-flammable wastes.

CONSISTENCE

Class I - liquid wastes,

Class II - semi-solid wastes (of the consistence of pulp, slime, paste, dough, etc.),

Class III - solid, dusty and loose wastes,

Class IV - Solid, coarse-grained wastes of the consistence of wet earth,

Class V - solid wastes, rocky, lumpy, solidified material.

WATER-SOLUBILITY

Class I - very easily soluble wastes; in the standard test 90-100 per cent of the mass are dissolved,

Class II - easily soluble wastes, 10-90 per cent of the mass,

Class III - moderately soluble wastes, 1-10 per cent of the mass,

Class IV - slightly soluble wastes, 0.1-1.0 per cent of the mass,

Class V - practically insoluble wastes, less than 0.1 per cent of the mass.

COMPOSITION OF WATER EXTRACT

Class I - standard water extract contains substances of the first toxicity class in concentrations exceeding 0.01 g/m^3 ,

Class II - water extract contains substances of the first toxicity class in concentrations lower than 0.01 g/m^3 and substances of the second toxicity class in concentrations exceeding 0.1 g/m^3 ,

Class III - water extract contains substances of the third toxicity class in concentrations exceeding 10 g/m^3 ,

Class IV - water extract contains substances of the third toxicity class in concentrations lower than 10 g/m^3 and substances of the fourth toxicity class in concentrations exceeding 10 g/m^3 ,

Class V - water extract does not contain any harmful substances.

VOLATILITY

Class I - very easily volatilizing wastes containing substances with a volatility index I_v lower than 5, which constitute more than 1 per cent of the total mass,

Class II - easily volatilizing wastes containing:

a/ substances of $I_v < 5$, which constitute less than 1 per cent of the total mass,

b/ substances of $I_v = 5$ to 50, which constitute over 1 per cent of the total mass.

Class III - moderately volatilizing wastes containing:

a/ substances of $I_v = 50$ to 200, which constitute over 1 per cent of the total mass,

Class IV - slightly volatilizing wastes containing:

a/ substances of $I_v = 50$ to 200, which constitute less than 1 per cent of the total mass,

b/ substances of $I_v = 200$ to 2000, which constitute over 1 per cent of the total mass,

Class V - wastes with no volatile components or wastes containing substances of $I_v > 2000$.

REACTIVITY

Class I - wastes containing substances which may react with water, air or soil to yield:

a/ first-class-toxicity products; degree of reaction, > 0.1 per cent of mass of the waste,

b/ second-class-toxicity products; degree of reaction, 90 to 100 per cent of mass.

Class II - wastes containing substances which may react with water, air or soil to yield:

- a/ first-class-toxicity products; degree of reaction, < 0.1 per cent of mass,
- b/ second-class-toxicity products; degree of reaction, > 1 per cent of mass.

Class III - wastes reacting with water, air or soil to yield at most third-class-toxicity products; degree of reaction, > 1 per cent of mass. The reaction products may be by a factor over 50 per cent easier water-soluble or more volatilized than their substrates.

Class IV - wastes reacting with water air or soil to yield:

- a/ third-class-toxicity products; degree of reaction, < 1 per cent,
- b/ fourth-class-toxicity products; degree of reaction, > 1 per cent.

The reaction products may be easier water-soluble or more volatilized than their substrates, but not more than by a factor of 50 per cent.

Class V - inactive chemical wastes with no constituents to react with water, air or soil.

CORROSIVITY

Class I - highly aggressive wastes:

- a/ liquid wastes exerting a corrosive action to h_a -class concrete and/or contributing to corrosion of low-carbon-steel (0.2% C) at a rate of over 10 mm/a at 293 K,

- b/ semi-solid and solid wastes the water extract of which fulfil the conditions of a/.

Class II - aggressive wastes:

- a/ liquid wastes exerting a corrosive action to m_0 -class concrete and/or contributing to corrosion of steel at a rate of 1 to 10 mm/a,

- b/ semi-solid and solid wastes the water extracts of which fulfil the conditions of a/.

Class III - moderately aggressive wastes:

- a/ liquid wastes exerting a corrosive action to l_{a2} -class concrete and/or contributing to corrosion of steel at a rate of 0.1 to 1.0 mm/a,

- b/ semi-solid and solid wastes the water extracts of which fulfil the conditions of a/.

Class IV - weakly aggressive wastes:

- a/ liquid wastes exerting a corrosive action to l_{a1} -class concrete and/or contributing to corrosion of steel at a rate of 0.001 to 0.1 mm/a,

- b/ semi-solid and solid wastes the water extracts of which fulfil the conditions of a/.

Class V - non-aggressive wastes.

Disclaimer

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HAZARDOUS WASTE MANAGEMENT TECHNOLOGY IN ITALY

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ABSTRACT

The problem of managing hazardous waste is not a new one for Italy. Despite that, however, it is only recently that a law regarding this matter has been approved. Problems being faced presently include implementing the law and setting up a technology sufficiently advanced and economically feasible for the entire system. Up to the present, the existing technology has been for the disposal of urban solid waste and sludges from the treatment plants and those already familiar to the chemical industry. Other methodologies have been established specifically for the disposal of toxic waste. In that field, a service industry is being developed in Italy which supports and often collaborates with municipal authorities. Transfer, transport, general policies for management and methods of disposal, as well as research requirements, are currently being studied.

INTRODUCTION

Europe produces 2,000 million tons of solid waste, 20 of which are toxic and hazardous. Only 30% of this is subjected to treatment; the rest is disposed of in so-called 'controlled dumps'. In Italy, it is estimated that about four million tons of toxic and hazardous materials are produced annually. Out of that quantity, it is presumed that 25% is adequately treated and disposed of. The Ministry for the Environment recently stated that, "There exists an urgent necessity to protect the environment from being submerged and destroyed by the residue of the productive system".

The problem of hazardous solid waste was dramatically brought to the public attention for the first time in Italy, at twelve-thirty-seven, on July 10, 1976, with the disaster at Seveso. At that time it was the regional authorities of Lombardy who had to handle the problem of reclamation of an area of 52 hectares seriously contaminated by an accidental leak of a dioxine cloud from an industrial plant. The problem was solved by creating two enormous dumps for the

contaminated earth, which amounted to 250,000 m³.

The first international conference on solid waste, sludges and residual materials was held in Rome in 1981 in an atmosphere of cooperation between Italy and the United States. It was followed by another in Philadelphia in 1983 and another in Alexandria, Egypt in 1985. The agreement of cooperation was later officially underwritten in Washington. The sponsors of that first conference were the EPA, DOE and ASTM.

LEGISLATION

Shortly after December 15, 1982 the first law on solid waste disposal was published, and Decree No. 915 of September 10, 1982 became law.

Following that Decree, on September 13, 1985, regulations were published for the first application of Article 4 of said Decree (No. 915), which in effect outlines the limits of jurisdiction of the national government.

The decree regarding solid waste (urban, industrial, hazardous and toxic), added to the existing government regulations on air and water pollution control, specifies the provisions to be made by national, regional, provincial and municipal authorities.

They are as follows:

The national authority must

- establish general criteria for waste disposal methods;
- establish the means to be adopted to avoid an increase in refuse and waste;
- coordinate regional programs.

The regional authorities must

- draw up organizational plans;
- authorize disposal sites;
- approve treatment plants.

Provincial authorities are in charge of control.

The duties of municipal authorities include urban and civil waste disposal.

Operating criteria, based on EEC guidelines include:

- authorization for landfilling (characteristics of area, types and maximum quantities of waste, duration and recovery of area);
- cost of refuse/waste disposal to be charged to the producer of waste;
- authorization of collection, transportation, temporary storage, processing and final storage of toxic and hazardous waste in controlled areas. It is compulsory for producers and

transporters of waste to maintain a register, and an identifying receipt must accompany waste during transportation.

Finally, a fine of up to five million Lire and one year's imprisonment are the penalties for non-compliance with the law.

A definition of toxic and hazardous waste (for which the law provides special regime and severe penalties) can be had from the three following suppositions:

1. The waste contains, or is contaminated by, one or more of the 28 classified groups of substances listed in the attached Decree 915.
2. Those substances are present in such quantity and/or concentration as to constitute a danger to human health or the environment.
3. The technical parameters used to define the characteristics of the toxic and hazardous waste have been determined by an apposite interministerial committee.

As Sanitary Legislation Act 833/78 provides for the creation of health conditions uniform throughout the national territory, the concept of toxic waste obviously must also be uniform and valid throughout the country.

The provisions of the law require that the interministerial committee follow strict criteria of rigid classification in determining the presence of the 28 classes of toxic and hazardous compounds listed. That classification presents serious difficulty in analysis and

consequently objective difficulty for waste producers and control agencies. To overcome these difficulties, clear scientific criteria should be adopted for determining limits of harmfulness. Similar criteria have already been applied on an international level, as well as technical requisites and operative procedures for disposal sites for toxic and hazardous waste, adequate for the protection of the environment and public health requirements. Regulations for the moment take into consideration only compost production, recovery of landfill biogas and incineration, however leaving space for the utilization of other techniques. Following the example of other countries, a classification system for toxic and hazardous waste is also foreseen based on the source of the waste. Also provided by the law is the producer's right to prove the absence of toxicity in waste material following previously prescribed procedure.

CRITERIA OF ACCEPTABILITY FOR WASTE DISPOSAL TECHNIQUES

The law intends to "provide the formulation of basic criteria and technical guidelines for the disposal of waste in general, as well as provide general criteria for authorizing the disposal of toxic and hazardous waste".

It also states that "actions permitting the quantitative reduction of waste introduced into the environment and the lowering of the level of harmfulness of the same as regards man and the environment are concurrently imperative for the implementation of the general terms of Decree No. 915".

Such actions can be set out as follows:

- a) intervention in the production cycle and phases of distribution and consumption, with the scope of limiting the formation of waste in the environment and during the phases themselves;
- b) intervention during the various phases of waste disposal, with the scope of recovering waste, materials and sources of energy;
- c) intervention for the improving of efficiency in the recovered materials markets and the expansion of the markets themselves;
- d) intervention to increase the use of recovered materials during the production cycles and in the construction of works.

The resolution cited also defines general criteria for disposal, as follows:

"The choice of system, technology and technical means to be used must be based on a comparative evaluation of the different solutions which are technically and economically feasible, keeping in mind, above all, the imperative of avoiding a negative impact on man or his environment.

Keeping in mind such criteria, preference is made for systems which ensure a considerably higher level of recovery of materials and energy for which there could exist concrete possibilities for commercialization and recycling."

The law also specifies the phases which allow a disposal of waste within limits imposed by hygienic/health requirements and the protection of the environment. They are: collection, treatment, definitive disposal and interventions on the release of solid, liquid or gaseous substances resulting from the preceding phases and the secondary operations of manipulation and transfer.

The reduction of operative costs is obviously a matter of optimum localizing of the treatment plants. This could be done by intermediate stations. Such localization would also take into consideration the position of the landfill sites where the residues are to be disposed of definitively.

TREATMENT CENTERS

Presently, in Italy the "treatment centers", in consideration of both transport costs which are relatively contained due to the high concentration of sludge and residual materials, and the particular difficulties met with in home treatment, are consolidating and forming coalitions of public and private firms. Internally, the operations carried out are those typical to chemical engineering, such as the various operations of transformation (such as chromates, cyanides, phenols) and those of separation (such as filtration, decantation, extraction, centrifugation, distillation), and so on.

The processes utilized are chemical, physical and biological, and are conveniently integrated. Elimination of organic residual substances when possible is done by means of combustion and landfilling preceded when necessary by stabilization processes.

The major problems as regards the activity of such centers are mainly:

- a) analytical control in real time of the different lots of material introduced;
- b) the computerization of all administrative and technical operations;
- c) the search for new means of treating the different residues.

DEVELOPMENTS

New from the technological point of view are the systems for stabilizing the landfills by means of controlled leachate collection in aerobic conditions. The advantage in this type of center is the possibility of a more efficient public control. The advantages for the producers of residues are, in addition to a more simple operation, of an economic and financial order. A major problem presently being confronted concerns the localization of the dump sites. Procedures for environmental impact have not yet been introduced into Italian legislation, and there exist no public participation programs, such as the siting boards encouraged in the U.S. with authority to approve or deny permits for waste facilities.

Following are the findings of a workshop recently conducted at Genoa University:

In this sector, in Western Europe, there is no clear-cut "polluter pays" principle. It would be advisable to define a more equitable system of financing. Regarding the transfer of waste over national borders, the most suitable control mechanisms are:

- procedures for "formal contracts for work";
- procedures for informing authorities in time to permit prior agreement;
- clearly defined procedures for exporter-importer approval;
- simple, effective documentation systems;
- a system for central records control.

Policies for waste control management could be improved by providing:

- a licensing system for the site;
- a licensing system for waste transporters;
- a system for monitoring and surveilling the licensed operations;
- a system for identifiable legal constraints on site management, transporter and discharge of waste;
- an implementation of effective national and international planning operational Codes of Practice.

Further development would also be advisable for methods of disposal. The principal disposal route is landfill. Cost-effectiveness must be determined by each individual case. Industry operates on its own survival profit policy. It might be wise to allow it to determine its own processes for recycling and recovery. However, that should always be within the limits imposed by the safeguarding of the environment.

Research presently being conducted falls into three categories:

1. Data and Information
2. Definition of Waste Difficulty Levels
3. New Processes

A generic listing of difficult waste materials should be available, instead of one which lists individual compound properties. Research on disposal should also relate to disposal groups.

CONCLUSION

It might be added, in closing, that in the interests of international scientific cooperation, and the obvious benefits which would result for all concerned, it is to be hoped that in the near future new life be given to the on-going agreement between Italy and the United States.

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MANAGEMENT OF HAZARDOUS WASTES IN EGYPT, AN OVERVIEW

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Statutory definitions of hazardous waste used by various countries reflect not only the nature of the environmental problems, but also the social, political and economic conditions of the countries concerned. When attempting to define hazardous wastes they lie in one of the basic categories:

- a) Short term acute hazards, such as acute toxicity by ingestion, inhalation or skin absorption, corrosivity or other skin or eye contact hazards or the risk of fire or explosion, or
- b) Long term environmental hazards, including chronic toxicity upon repeated exposure, Carcinogenicity (which may result from acute exposure, but with a long latent period), resistance to detoxification process such as biodegradation, possibility of underground or surface waters contamination or aesthetically objectionable properties such as offensive odors.

Wastes with these properties may be products, side products, process residues, spent reaction media, contaminated plant or equipment from manufacturing operations, and discarded manufactured products.

The management cycle for any particular hazardous waste comprises its generation, transport, storage, treatment and final disposal. One approach to the problem of adequately defining what constitutes a hazardous waste is to draw up a list of known wastes that present no significant short-term handling or long-term environmental hazards, and to define hazardous wastes by exclusion i.e. as any wastes not listed. This list is based on the criteria that the waste should not contain any hazardous quantity or concentration of any poisonous, noxious or polluting substances. Clearly many hazardous characteristics, such as corrosivity, flammability, and high acute toxicity by ingestion, inhalation or skin absorption, will cause potential problems at all these stages.

By contrast, many wastes that offer no significant short-term handling hazard may cause severe disposal problems due to their physical or chemical properties (1).

In developing nations, the management of hazardous wastes can face its biggest enemy, which is essentially the ignorance of the extent of the problem and consequently the unwillingness to take the proper measure to execute the management policies.

Proposed Plan for Hazardous Waste Management in Egypt:

Egypt now is in the industrialization era. Lots of raw materials are imported to suit the requirements of the vast array of industries localized in the different metropolitan areas, such as Alexandria Cairo, as well as those scattered all over the Nile valley.

Lack of proper industrial planning has led to heavy concentration of industry in Alexandria's metropolitan area, with a significant high level of pollution as all effluents are discharged without any treatment. Organic and inorganic chemical industries have contributed measurable amounts of heavy metals and toxic substances cyclic and alicyclic compounds. An example of the industrial loads discharged by the Alexandria Metropolitan area are shown in Tables 1,2 by Hamza (1983).

The national approach to establishment, organization and implementation of a system for the management of hazardous waste should reflect the constitution, legal system and political objectives of the country. The major part of industry in Egypt is owned by the government and, at the same time, the government is responsible for avoiding the random provision and distribution of disposal facilities and for ensuring the environmentally acceptable treatment and disposal of hazardous waste.

This situation posed a double financial and executive burden on the government. This basic idea was taken into consideration when planning for a management policy.

Survey Hazardous Materials:

An essential requirement for the realistic planning of hazardous waste management is an adequate knowledge of the quantities and types of waste produced. The first step should be collection and evaluation of existing data on the distribution of wastes generated and on the total amount of waste requiring treatment or disposal.

Parallel with this exercise, a review of the existing waste treatment and disposal facilities is essential.

The data collected during this stage, based on government agencies information, was not sufficient to give a full picture about the realistic situation. Deviations are due to the following factors:

- 1) Lack of proper housekeeping in the Egyptian factories leading to a higher percentage of raw material losses in the waste with a consequent raise in the organic and inorganic loads in the final effluent of the plant. This is obvious in practically all canneries and food processing plants.
- 2) The old technology used in the already established plants allows for mishandling of chemicals and raw materials as well as products. A vivid example is the discharge of mercury to the sea from a caustic soda plant using the electrolytic process in Alexandria, where ten tons of mercury find their way annually into the sea.

- 3) The dirty technology exported by developed countries to avoid the high cost of labor and the skyrocketing expenses of toxic waste handling and treatment due to the presence of strict applicable laws. Processing of dyes and intermediates by Ismadye company is another dangerous example.
- 4) Lack of proper knowledge about the extent of hazards created by the different components, from the petroleum fuel used in boilers to the flammable solvents and to the carcinogenic chlorinated hydrocarbons produced by pesticide producing companies.
- 5) Socioeconomic factors leading to the carelessness of human operators and their unwillingness to adopt better production and operation systems.

The above listed factors make the standard procedures of sending questionnaires and depending on the data supported by the governmental agencies a false base.

The more proper methodology for developing countries would be to convince the industrial management authority, in the different plants, that the government will help them overcome their problems and that, the more positive and accurate the response of the industry, the better their chances to get first priority in the allocation of funds for solving their hazardous waste problems.

Training programs carried out by academic organizations will help in creating awareness in the different industries about the extent of hazard each specific industry is creating for its surrounding environment, of which the industry personnel are a part.

Upgrading the technical-level awareness as to the size of the problem will make the reporting of realistic information about the waste a more accurate process as operators of all industries are the best people to give a true picture of the pitfalls of the technology used in their plants.

Surveying has to be carried under the supervision and with the help of environmental organization staff, not with the attitude of picking on the mistakes, but with the idea of helping the industry to solve its problems with hazardous wastes.

Surveying is planned to be taken in the following steps:

- 1) Contacts with the ministry of industry and its affiliated industrial organization for the allocation of industrial plants and categorization of industries.
- 2) A questionnaire has been prepared to be sent to all plants as a request from the ministry with the concept of sizing the problem and the needed budget for its solution.
- 3) Academic organizations in different metropolitan areas will be responsible for verification of the collected data and, in case of a feeling of unrealistic information (which can be the case in most instances), the surveying group has to visit the plant and work to correct the data, together with management, raise their awareness of the magnitude of the problem, and discuss the best way to approach the government to seek financial support for the needed on-site treatment or methods of final disposal for their hazardous wastes.

A data bank for the different sources of industrial pollutants can be started and fed with all this basic information. This will help in evaluation of new technology as far as its hazards and the best site for its allocation, as well as the best way to handle its toxic or hazardous effluents as generated in the selected site.

Waste Disposal Plans:

Comprehensive waste disposal plans can be prepared based on the collected information. Plans have to be prepared to suit the requirements of each governorate where industrial centers are located. The following subject areas will be taken into consideration to be covered:

- 1) The kinds and quantities of hazardous wastes expected to be treated and disposed of in the area, including wastes generated by the governmental authorities responsible for handling the combined domestic and industrial effluents in certain metropolitan areas, as in Cairo and Alexandria.
- 2) The number, type and location of receiving centers and pretreatment facilities.
- 3) Management of the waste disposal facilities, as owned by the government, and the best administrative measures to be pursued to ensure success in their operation.
- 4) Proposed methods of disposal and/or recycling. The economy of developing countries has to be taken into consideration. This area is also inviting for foreign technology to find a good market for treatment and/or recycling units.

- 5) Identification and location of special facilities suitable for individual particularly-hazardous wastes. The governorate must locate those facilities as far as possible from residential areas and also prevent unplanned housing projects from coming so close to those plants that, due to ignorance, there could be exposure hazards to the inhabitants.

Characteristics of Sites Suitable for Hazardous Waste Disposal:

Due to the limited funding that can be allocated for hazardous waste disposal in Egypt, it is advisable to join both domestic refuse and industrial hazardous waste disposal in one facility owned and operated by governmental agency.

Large public-sector firms, as in the case of textile plants, steel mills, paper-processing firms and especially organic and inorganic chemical processing industries, can handle their own disposal sites and facilities. Big industrial complexes comprising varying industries as in Helwan, Shoubra, Kafr El Dawar, El Seiuf, Moharrem Bey and El Max, can operate an incineration facility to get rid of their combustible hazardous wastes.

Problems may arise even at the stage of selecting the location, with objections raised by the industries as being too far or not convenient for some of them. This can be overcome by the governmental authorities responsible for operating the site by charging variable rates based on the extent of toxicity, corrosivity, flammability, or carcinogenicity, as well as distance and cost to be paid by the producing firm. On the other hand, levying taxes on the chemical

products and on producers will help raise funds for operation and maintenance of hazardous wastes handling facilities. This will also prompt producers to limit their wastes through better housekeeping and to try to recycle and produce beneficial side products from their wastes.

This collected fund will help in hazard waste facility purchase and site preparation, as well as its operation and maintenance.

General subsidies given to producers and manufacturers should be avoided because they may remove the economic incentive to recycle wastes or to recover value from them.

Governmental funds can only be resorted to when there is a need to improve the technology to adapt to a new hazardous waste generated by a newly introduced process.

Landfill is the best technology that can be afforded by developing countries such as Egypt. The physical factors of greatest concern are the soil characteristics and groundwater conditions. For a collection and processing site, the most important considerations are the industrial burden already existing in the area.

Boreholes of the soil at the selected sites will show the level of groundwater and its salt content. This will dictate the quality of the hazardous wastes to be disposed at that site by surface spreading or controlled dumping.

Legal and Administrative Requirement

A comprehensive system for the disposal of hazardous waste will not develop unless its basic requirements are prescribed and dictated by law.

Assessment of the existing laws and regulations in Egypt showed clearly that the concept of health-hazard effects of toxic or hazardous constituents is not really understood. Parameters like those describing the biological and chemical amenability to degradation are listed.

Hazardous waste legislation will have to impose duties on the general public, and the present law should be modified to impose those duties.

The technical aspects of hazardous waste management should, therefore, be governed by statutory or administrative regulations, as appropriate.

The most important task for hazardous waste management legislation in Egypt is the designation of responsibility for disposal. Public authorities can handle it themselves. This system has a basic disadvantage of being excessively bureaucratic and inflexible and may not be adequately sensitive to cost benefit relationships or to local public or industrial needs.

The major advantage would be the assurance of having a running facility that can accommodate different wastes to suit the environmental requirement.

The legal responsibility for the proper disposal of waste should remain with the waste generator who should be responsible for the following:

- The choice of proper transport and disposal methods for the waste in question.
- Avoiding, minimizing, and recycling wastes as far as is technically possible and economically reasonable.

Table 1 Estimated waste loads of pollution-contributing industries in Alexandria Metropolitan Area

Industry	No of Plants	Discharge	Flow, ML/d	BOD	COD	O&G	SR	VR	P	N
Pulp & Paper	2	S	93	83462	103356	1817	56069	80635	302	210
Paper Conversion	3	LSD	5	3679	7379	1996	7543	7454	43	125
Textiles	13	LSD	37	19895	37877	3114	29949	41312	116	123
Dyes	1	S	4	983	580	48	366	447	31	25
Fertilizers	1	S	30	252	1392	276	558	1032		
Steel	1	Se	13	520	1430	170	585	890	86	43
Oil & Soap	8	Se,C	32.5	30935	61943	9800	44685	51202	67	56
Tyres	1	Se	4.3	504	1260	286	940	1092	54	43
Retineries	2	S,L	230	12615	41875	10740	24370	44770	366	374
Chemical (Inorganic)	1	S	35	10850	22035	3215	39050	35600	741	195
Tanneries	6	S	16	2688	4109	405	13600	11424	431	243
Power	2	C	324	7662	12022	11248	15606	12987	135	128
Match	2	L	1.1	496	862	98	1085	1452	82	286
Electronics	1	D	0.5	138	269	59	320	356		2.1
Refractories	1	D	0.5	147	297	171	806	716		
Plastics	1	D	2.5	788	725	395	713	905	113	194
Bottling	2	Se	1.9	484	693	89	256	432	60	93
Canning	2	D	4	3000	4264	177	1137	2258	54	31
Dairy	1	D	0.8	1240	3660	950	2982	6055	25	30
Yeast & Starch	3	SE,L	3.2	2440	3360	106	1950	2130	86	51
Brewery	1	Se	1.2	386	184	41	160	192	16	06
Poultry	1	D	0.5	429	583	51	681	693	25	3.1
Pharmaceuticals	1	Se	0.9	576	936	39	108	475	4.5	0.7
Total	57		828	184235	311591	45330	243519	304509	886	1094

(1) L = Lake S = Sea Se = Sewer C = Canal D = Drain

Table 2 Average analysis of trace metals in selected industrial effluents

Source	Zn	Cu	Ni	Cr	Cd	Fe	Mn	Pb
Copper Works	594	450	388	ND	ND	1392	144	209
Canning	1800	30	5	20	0.5	2200	340	30
Dairy	1144	185	234	210	0.5	3275	355	255
Tyres	6285	400	ND	150	0.5	2550	205	45
Textiles	101	107	198	ND	2	320	119	102
Paper Conver.	113*	220	20	360	3	4050	480	410
Electronics	6250	70	ND	50	8	1525	373	255
Oil & Soap	5550	95	60	30	0.5	3625	445	285
Tanneries	2133	603	545	127*	715	14*	979	1238
Inorganics	381	355	475	ND	29	1776	216	527
Foundry	8400	290	30	460	3	21800	630	260

*Concentrations in mg/l

ND= Not Detected

- Correct declaration and proper labeling according to the newly set legal requirements.

Control of Hazardous Waste Management

One of the basic legal requirements for the implementation of a reliable system of hazardous waste management is the establishment of comprehensive control mechanisms.

There are three basic groups of measures to control hazardous waste management.

The first step is the control of waste generating process. This should be controlled by the Ministry of Health legal requirements aimed at avoiding or minimizing hazardous waste generation such as the following:

- Proper choice of foreign technology to ensure better raw materials, operations and maintenance procedures.
- Recycling of waste into beneficial by-products.
- On-site treatment of waste for mass reduction, dewatering, detoxification or change into an immobile and/or chemically inert form.

The second step of the control system should aim at licensing procedures for potentially hazardous activities. This means that all places where hazardous waste is stored, treated or disposed of should require a license which should be obligatory by law.

The third essential step is a comprehensive system of notification establishing a link between the different activities.

The above management plan can be used, not only in Egypt, but in all developing countries where the concept of industrialization is highly appealing with no precautions for its hazardous wastes.

Supporting Literature

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Disclaimer

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NATURAL GEOCHEMICAL ATTENUATION OF CONTAMINANTS CONTAINED IN ACIDIC SEEPAGE

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ABSTRACT

Present-day environmental regulations require that waste disposal facilities be designed and engineered with redundant seepage-control systems. Despite the best efforts, there is a possibility of contaminant loss from such facilities. In this case, natural retardation mechanisms will be important in controlling the migration of pollutants.

A conceptual geochemical model has been developed to explain the interaction of acidic seepage with natural soil materials. The model is based on numerous laboratory tests and field investigations of the saturated and vadose zones at uranium, copper, and phosphate milling and processing sites throughout the United States, Canada, and Australia. Principal geochemical reactions are identified and case histories are presented to illustrate the degree of natural control on contaminant migration.

Based on the observed, predictable order of contaminant migration, it is possible to develop a cost-effective system of phased monitoring which incorporates the geochemical model, reduces the monitoring parameters, and yet provides equal or greater levels of environmental protection. Suggestions for such a monitoring program are advanced.

INTRODUCTION AND PURPOSE

Present-day hazardous waste regulations require that waste disposal facilities be designed and engineered with redundant seepage-control systems. The best engineered facilities are not truly "impermeable" and can develop leaks over long periods

of waste containment. When the leaks occur, the natural retardation mechanisms provided by underlying soils, sediment or bedrock will constitute the control on the spread of hazardous constituents contained in the waste.

Many hazardous wastes from mining, milling, and processing operations are acidic solutions which are generated by the reaction of mineral acids such as sulfuric acid with a raw material. When such acidic waste escapes from a containment facility and penetrates the underlying soil or sediment, a complex series of geochemical reactions can be initiated which may immobilize many of the hazardous constituents in the waste. Laboratory and field studies have provided valuable information on the various geochemical reactions which take place and on the relative importance of each of these reactions. The studies have shown that predictions can be made about the rate of advance of various contaminants. The predictions are based upon the chemical properties of the waste solution and upon the geochemical properties of the underlying geological material. Relying upon this predicted order of contaminant migration, monitoring programs can be developed which provide for a more cost-effective as well as a more environmentally sound monitoring scheme which utilizes the more rapidly advancing constituents to alert the operator of the need for increased monitoring efforts.

This paper describes some of the important geochemical reactions that take place, presents a conceptual model for the interaction of acidic seepage with natural material, and provides suggestions for a phased monitoring program which recognizes that geochemical attenuation is likely to occur to some extent in all natural media.

GEOCHEMICAL PROCESSES

Numerous investigations have provided insight into the geochemical processes that are at work when acidic seepage penetrates the subsurface. An excellent description of the ground water mobility of various contaminants is provided by Cherry, Shepherd, and Morin (1). Another discussion of contaminant migration, as it relates to the phosphate industry, is provided by Rouse and Bromwell (2). Numerous investigations have been published for uranium, base metal, precious metal, and phosphate operations throughout the United States and Canada (3, 4, 5, 6).

The geochemical processes that are at work as acidic solutions come in contact with natural materials are extremely dynamic. Some of the reactions tend to remove contaminants, while others exchange one contaminant for another, or actually add contaminants into the flow system. These dynamic processes must be better understood before water-quality data can be correctly interpreted or before effective remedial measures can be designed.

By far, the single most significant geochemical process that takes place between acidic seepage and natural materials is the reaction and dissolution of carbonate minerals. Hydrogen ions in the acidic solution will react with calcite or other carbonate minerals which may be present in the underlying soil, sediment, or bedrock. In the course of the reaction, hydrogen ions are consumed to form

bicarbonate and the acidity of the seepage is neutralized.

Calcite dissolution and acid neutralization can trigger a host of geochemical reactions. These reactions can effect not only the quality of ground water, but also the geotechnical properties of the subsurface. For example, dissolution of calcite introduces calcium ions into the seepage system. If the seepage solution is enriched in sulfate content, secondary sulfate minerals such as gypsum or anhydrite may precipitate. Since secondary gypsum occupies more volume than the previously dissolved calcite, a reduction in subsurface permeability may occur.

On the other hand, neutralization of an acid seepage will establish pH conditions which are favorable to the functioning of geochemical mechanisms such as ion-exchange, sorption, and precipitation which tend to remove potential ground water contaminants from solution. Precipitation of heavy metal hydroxides is one mechanism which is initiated by the calcite dissolution and acid neutralization process. The precipitation is pH dependent and has been studied by a number of investigators. Rouse (7) presents a summary of the process and describes how various metals are sequentially removed as a result of increasing pH. Iron is the earliest metal hydroxide to be precipitated with increasing pH, followed in turn by aluminum, copper, zinc, and finally manganese. In a recent ground water investigation of the Globe-Miami area of Arizona, several such sequential precipitation plumes have been observed downgradient of the local mining operations (8).

EVIDENCE FOR GEOCHEMICAL ATTENUATION

Many studies have provided data on the geochemical reactions that have been described above. This source of data comes from column test results obtained in the laboratory and from field investigations of actual contamination sites.

Column Test Results

Column tests, such as the one depicted in Figure 1, are often conducted in order to predict what geochemical interactions will occur between a certain waste solution and the natural materials that the solution may contact. The

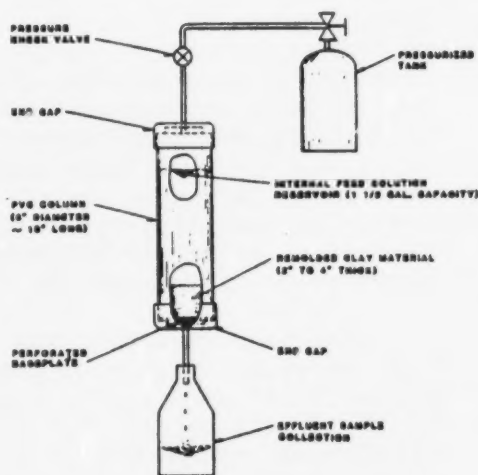


Figure 1. Laboratory column experiments to predict geochemical interactions between waste solutions and natural materials.

objective of the column test is to percolate the waste solution through the natural material, to collect and analyze the effluent, and to compare the composition of the effluent with the original composition of the waste solution.

Chemical and radiological analyses of two effluent samples from a series of column experiments are presented in Table 1. The data serves to illustrate the functioning of geochemical reactions which tend to remove potential ground water contaminants from a waste solution.

Both columns from the test series were packed with very similar clay-bearing material, and both columns were exposed to the same acidic waste from a uranium milling operation. The effluent samples whose compositions are profiled in the table represent about the fifth pore volume of waste solution throughput. The principal difference between the shale material in column A and in column B was calcium carbonate content. The shale material in column A was highly calcareous, and capable of effectively neutralizing the acidic pH of large volumes of uranium mill-waste solution. By neutralizing the acidity, optimum pH conditions are established for geochemical removal of ions from solution. Many of the geochemical mechanisms are most active in a pH range of 4.5 and 9.0.

Field Investigation Results

A number of investigators have described the reactions of acidic seepage with natural materials downgradient of a contamination source. These

TABLE 1. ANALYSES OF EFFLUENT SAMPLES FROM TWO COLUMN TESTS

CONSTITUENT	COLUMN A	COLUMN B	URANIUM WASTE
Effluent pH	7.7	3.5	1.8
<u>Concentration (g/l)</u>			
SO ₄	12.4	19.7	25.6
HCO ₃	1.6	0.0	0.0
Na	3.42	3.37	3.40
Ca	0.38	0.48	0.55
Mg	1.42	2.22	1.52
Al	0.0	0.42	1.01
Si(in mg/l)	7.9	37.	57.
<u>Concentration (mg/l)</u>			
As	0.12	0.28	1.51
Cu	0.07	14.9	34.5
Fe	0.44	338.	762.
Mo	<0.10	<0.10	2.89
Pb	<0.02	<0.02	1.0
Se	0.14	0.14	0.24
V	<0.10	83.5	501.
Zn	0.13	6.9	5.5
U ₃ O ₈	0.32	1.47	3.88
<u>Concentration (pCi/l)</u>			
Ra 226	0.2±0.3	9.1±2.3	63±7
Th 230	2.7±5.3	3900±200	82000±1000
Pb 210	0.0±4.6	4.7±3.9	1930±30
Po 210	0.8±3.9	8.0±12	3300±200

investigations clearly support the findings of laboratory column tests.

One of the most extensive geohydrological and geochemical investigations focused on a 500 square mile area in eastern Arizona which was impacted by contaminant migration from natural mineralized areas and from extensive copper mining and milling operations (8). Since the water-bearing bedrock contained low concentrations of

carbonate minerals, an extensive contamination plume was formed downgradient of the source of the contamination. Such an extensive, elongated plume enabled the definition of various contamination zones. Pumping a non-contaminated aquifer underlying the contamination plume resulted in the migration of contaminants into the producing aquifer. Chemical breakthrough of various constituents into the producing aquifer was in accordance with the order of appearance predicted in the column tests.

Recent monitoring near gold-mill tailings in South Dakota has indicated that a similar order of contaminant appearance is in effect in unsaturated as well as saturated zones.

Investigations of a man-induced perched water system underlying an acidic uranium mill tailings pond in western Colorado confirmed the existence of acidic water similar in composition to seepage that had undergone geochemical modification (9).

An evaluation of radionuclide migration below the base of an Australian uranium mill evaporation pond displayed a strong positive correlation between radionuclide content and the acidity of the material. This allowed for the development of a rapid field inspection technique which can be used in reclamation efforts, without the need for time-consuming laboratory assays (10).

At another uranium mill in eastern Washington state, monitor wells within 100 feet of a tailings pond did not detect elevated levels of metals or radionuclides, despite a seepage rate of approximately 1500 to 2000 gpm over a 2 year history.

Downgradient wells contained lower radium concentrations than upgradient wells, as a result of gypsum precipitation and radium coprecipitation (11).

During an investigation of ground water quality downgradient of a series of seepage ponds, data were generated which displayed an orderly progression of contaminant attenuation. Radium contamination was not above the EPA Drinking Water Standards, even in a monitor well drilled on the berm separating two of the ponds (12). Table 2 illustrates the range of chemical quality, and the sequential attenuation of contaminants for various wells.

CONCEPTUAL MODEL

The findings and conclusions from the various investigations described above provide sufficient background to develop a conceptual geochemical model for

TABLE 2. ANALYSES OF GROUND WATER SAMPLES FROM WELLS ALONG SEEPAGE PLUME, SHOWING SEQUENTIAL CONTAMINANT REMOVAL

CONSTITUENT	WELL CRP-8	WELL CRP-8	WELL CRP-8
pH	3.45	6.3	6.75
Concentration, mg/l			
TDS	146000	26100	7640
Bicarbonate	0	1970	805
Sulfate	83600	18400	5190
Chloride	5230	1310	354
Sodium	6300	970	270
Potassium	23	180	94
Calcium	230	530	270
Magnesium	16000	3500	780
Iron	2900	0.15	0.07
Manganese	510	23	2.7
Zinc	220	1.1	0.48
Copper	27	0.04	0.02
Cadmium	6.7	0.01	<0.01
Nitrate	20	145	40
Ammonium	549	760	383
Uranium	11	0.6	0.18

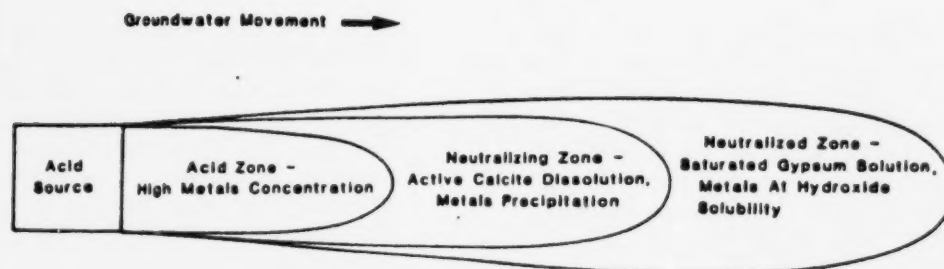


Figure 2. Conceptual model of geochemical zones in a contaminant plume.

contaminant movement and immobilization. This conceptual model is similar to the model which was suggested by Cherry, Shepherd, and Morin (1) and is based on the results of many laboratory column tests, as well as on the field experience of the authors at uranium, phosphate, copper, and gold mining sites throughout the United States, Canada, and Australia.

As an acidic waste percolates into the subsurface, geochemical processes begin to occur at the advancing front. Calcite dissolution and acid neutralization result in a movement of the reaction front. Depending upon the calcite content of the natural subsurface material, the acid front is slowed, and retarded in its down-gradient movement relative to the rate of the fluid travel. The advance of the acid front is controlled by the number of pore volumes of acid water that must react with a given volume of porous media to completely dissolve all of the calcite.

In effect, as the contaminant plume proceeds down-gradient, a total of three distinct zones will develop (Figure 2). The first zone, which

may be termed the "acid" or "core" zone, consists of ground water with a quality virtually identical to that of the source of the seepage. The water is characterized by extremely low pH, very high sulfate ion concentrations, and contains numerous heavy and toxic metals. In the acid or core zone all of the carbonate minerals present in the soil or bedrock have been dissolved. In soil or bedrock which is high in carbonate content, the acid or core zone often is only a few meters in extent. Well CRP-8 (Table 2) illustrates a well within the acid zone.

The second zone in the conceptual model is termed the "neutralizing zone" and is the area of active calcite dissolution and the formation of chemical precipitates including gypsum and the heavy metal hydroxides and carbonates. Water in this zone is characterized by high levels of some dissolved metals, in accordance with the sequence of metal hydroxide removal. The types of metals present can be directly related to the resultant pH of the solution. Well CRP-6 (Table 2) is a well located near the middle of a neutralizing zone.

Downgradient of the neutralizing zone is an area which can be termed the "neutralized" zone. Water in the neutralized zone is characterized by high concentrations of total dissolved solids, and is frequently saturated with respect to gypsum. Little, if any, calcite dissolution occurs in the area. Virtually all of the calcite originally in the soil or bedrock remains available for reaction. Well CRP-14 (Table 2) is close to the boundary between the neutralizing and neutralized zone.

PHASED MONITORING APPROACH

The accepted approach to monitoring is to analyze for a large number of constituents. Since there is a logical and predictable order for the appearance of contaminants as the contaminant plume advances, it is possible to design and operate a cost-effective monitoring program which recognizes that geochemical attenuation can occur and limits the number of constituents that are analyzed. Such a monitoring program can concentrate on identifying critical constituents to alert the operator of the need for increased efforts. In the area of the neutralized zone, the initial monitoring should consist of major ion analyses, with special attention directed at sulfate and total dissolved solids. There is no rational basis for heavy metal analyses so long as the water chemistry of the ground water is typical of background or of the neutralized zone.

The sequential order of contaminant appearance predicts that manganese and zinc will be the first of the common heavy metals to appear, followed in turn by copper, aluminum, and finally iron. For this reason,

once the sulfate concentrations indicate the proximity of the neutralizing zone, monitoring should begin for manganese and zinc. Only when these contaminants appear, the monitoring program should be expanded to include other metals such as iron or copper.

There are several important advantages of the phased monitoring approach. The program can be designed to be site specific, taking into consideration the chemical properties of the waste solution as well as the geochemical properties of the underlying geological material. The phased monitoring approach can be cost effective and can quickly generate water-quality data that are meaningful and instructive.

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PETROLEUM REFINERY SOLID WASTES: WHAT WILL WE DO WITH THEM?

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ABSTRACT

The objectives of this paper are to (1) provide an overview of the EPA Refinery Waste Characterization Study and the American Petroleum Institute (API) oversight program, (2) discuss some of the possible ramifications of the 1984 Resource Conservation and Recovery Act (RCRA) and possible new hazardous waste regulations, and (3) discuss some possible avenues that may be available for reducing the impacts of the potential new regulations.

Certain petroleum refinery wastes are listed by RCRA regulations, part 261.32 as hazardous wastes. These wastes are: (1) dissolved air flotation float (DAF) - K048; (2) slop oil emulsion solids - K049; (3) heat exchange bundle cleaning sludge - K050; (4) API separator sludge - K051; and (5) tank bottoms (leaded) K052. Waste streams K048, K049 and K051 are listed as hazardous because they contain hexavalent chromium and lead. Waste K050 is listed because it contains hexavalent chromium and K052 is listed because it contains lead. Other refinery wastes are hazardous only if they fail the Extraction Procedure (EP) toxicity test.

Some refineries dispose of these wastes by land treatment and are required to have a Part 264 Part B permit, and this permit requires that the Appendix VIII hazardous constituents be identified. The Office of Solid Waste is conducting a Refinery Waste Characterization Study. The major emphasis of this study is to identify waste characteristics of approximately 35 refinery waste streams (several of which are not currently hazardous waste) so that the results can be used for evaluating delisting petitions and Part B permit applications, and possibly for developing new hazardous waste regulations.

INTRODUCTION AND PURPOSE

The Resource Conservation and Recovery Act (RCRA) regulations issued May 19, 1980, 40 CFR

261 (1), listed certain petroleum refinery wastes as hazardous wastes. The wastes are: (1) dissolved air flotation float (DAF)-K048; (2) slop oil emulsion

solids - K049; (3) heat exchange bundle cleaning sludge - K050; (4) API separator sludge - K051; and (5) tank bottoms (leaded) - K052. Waste streams K048, K049 and K051 are listed as hazardous because they contain hexavalent chromium and lead. Waste K050 is listed because it contains hexavalent chromium and K052 is listed because it contains lead. Other refinery wastes are hazardous only if they fail the Extraction Procedure (EP) toxicity test.(1)

The Environmental Protection Agency (EPA) began conducting a Refinery Waste Characterization Study of waste streams generated at petroleum refineries in October 1983. The purpose of the EPA study is to characterize the five waste streams currently listed by RCRA regulations as well as other candidate streams that may contain hazardous substances and develop a data base to assist in evaluating delisting petitions submitted by refineries.

APPROACH

Most, if not all, petroleum refineries have submitted delisting petitions, for the five waste streams listed in 40 CFR 261, to the EPA because the concentration levels of hexavalent chromium and lead, as detected by the EP toxicity test, are far below the limits specified by 40 CFR 261. The EPA decided that they needed more data to evaluate these delisting petitions and that possibly other chemical parameters (metals and organics) should be evaluated to determine if refinery wastes should be classified as hazardous wastes. At the pre-

sent, refinery wastes, other than the five listed wastes, can be disposed in a non-RCRA waste disposal facility.

In October 1983, the EPA contractor began the Refinery Waste Characterization Study. The American Petroleum Institute (API) hired a contractor to oversee and evaluate the EPA study and conduct a parallel analyses program. The purpose of the EPA study is to identify potentially hazardous constituents in approximately 35 (Table 1) refinery waste streams (several of which are not currently hazardous waste). The Agency wants to classify the hazardous organic compounds in the refining wastes to determine if these wastes should be declared hazardous because of the organic compounds.

Eight refineries were selected and preliminary sampling and analyses were conducted on some or all of the waste streams listed in Table 1. Based on this preliminary testing, the Agency is considering whether to redefine the standards for regulating dissolved air flotation float and leaded tank bottoms based on their possible hazardous organic constituents as well as their metal content. The EPA also will determine whether to list refinery wastes in addition to the five types now regulated under RCRA. Additional sampling and analyses will be necessary before the EPA makes any final decision.

The waste listing studies were mandated by Congress in the 1984 RCRA amendments.(2) These amendments require the EPA to issue by November 1986 rules broadening the basis for

regulating wastes based on their constituents and to complete action by November 1986 on all delisting petitions requesting wastes be removed from RCRA controls.

The analytical program conducted by EPA and API contractor varied considerably from the past EPA Office of Solid Wastes approach of analyzing refinery wastes for EP toxic metals. While the past interest in the five wastes currently listed has been chromium and lead from the EP toxic extracts, the new analytical plan is far more extensive. Past experience has indicated that the current EP toxic procedure does not adequately evaluate metals in oily wastes; therefore, a new oily waste extraction procedure was developed and the extract was analyzed for both EP toxic metals and total metals. All samples were analyzed for a group of 12 metals and 95 organics. Several of the organic compounds could not be analyzed using existing techniques; therefore, new techniques were developed and will be published in the near future. The samples were analyzed for total as well as EP toxic metals using the new oily waste extraction procedure. Emphasis may be placed on total metals rather than oily waste EP toxicity during data evaluation by the EPA. The new oily waste procedure removes all water and oil from the sample before performing the existing extraction procedure. The EP oily waste test result consists of the composite analyses of the aqueous, oil and solid fractions. The organic analyses measured the total concentration of the 95 organic chemicals in the samples.

The results of the analyses described above will be used to determine if the five waste streams currently listed will remain listed. Some of the other waste streams (Table 1) may be listed as a result of this study. Considering the complex and extensive analyses that were performed, it was of the utmost importance that the samples collected be representative of the waste streams under study. The EPA contractor collected all samples under the observation of the API contractor and refinery personnel. Samples were split and analyzed by the EPA and API contractors. Results of this study are expected to be published by the EPA in the near future. These results are not available at this time.

Many refineries dispose of their wastes by land treatment and are required to have a 40 CFR 264 Part B. Permit and this permit requires that 40 CFR 261, Appendix VIII hazardous constituents be identified. The Appendix VIII list contains most organic chemicals known to man. In April 1984, an EPA memo(3) presented a list of Appendix VIII hazardous constituents suspected to be present in petroleum refinery wastes and a special analytical method for refinery wastes. The wastes listed are essentially the 12 metals and 95 organic chemicals analyzed during the EPA Refinery Waste Characterization Study.

This memo states "Because the design and management of a land treatment unit is based on the goal of attaining treatment of hazardous constituents (i.e., constituents listed in Appendix

VIII), it is very important that the presence of the constituents in the land treated wastes be accurately identified and quantified. This is best achieved through a comprehensive waste analysis for all Appendix VIII constituents. However, due to the cost and analytical difficulties associated with these analyses, many applicants have submitted requests to conduct analyses for some subset of Appendix VIII, which are 'reasonably expected to be in or derived from the wastes to be land treated.' To date, the majority of the wastes proposed for land treatment have been petroleum refinery wastes, specifically the listed wastes K048-K052."

The list provided in this memo is to be used until the results of the EPA study are available. This list is the same information that the EPA recently requested from all delisting petitioners.

PROBLEMS ENCOUNTERED

Two major problems were encountered during the course of the EPA study. These were: (1) development of a new extraction procedure for oily wastes and (2) development of analytical techniques sufficient to analyze for the 95 organic compounds.

A third problem exists for industry that is required to conduct the analysis for delisting or a Part B permit. The analytical techniques developed during the EPA study are not published and only two or three laboratories in the U.S. are currently able to use these techniques. Also, the cost of conducting

these analyses are expensive (\$1,500 to \$2,500 per sample).

RESULTS

Results of the EPA Refinery Waste Characterization Study are not available at this time. However, recently published data(4), obtained using these techniques, indicates that refinery wastewater sludges, as well as sludges from API separators and DAF units contain toxic organic constituents including benzene, toluene, benzo(a)pyrene, chrysene and pyrene. These data were the result of a delisting petition; however, one can assume that the results of the EPA study will identify the same and possibly more constituents that are toxic and cause more refinery wastes to be controlled by RCRA.

Table 1

LIKELY WASTE STREAMS FOR EVALUATION IN REFINERY INDUSTRY STUDY^(a)

Wastewater Treatment Residuals

- o Sludges Generated in the Gravity or Chemical Treatment of Refinery Wastewaters
- o Air Flotation Unit Float
- o Biological Treatment Sludges
- o Heat Exchange Bundle Cleaning Sludge
- o Flow Equalization Basin Sludges

Slop Oil Recovery

- o Slop Oil Emulsions
- o Slop Oil Tank Bottoms

Storage Tanks

- o Crude Storage Tank Bottoms
- o Gasoline Storage Tank Bottoms
- o Clarified Oil Storage Tank Bottoms

Lube Oil Production

- o Spent Solvents (especially Phenol, Demex, Di-Me and Other Chlorinated Hydrocarbons)
- o Solvent Rich Condensates
- o Treating Clays

Catalytic Cracking

- o Spent Catalyst
- o FCC Fines
- o Clarified Oil Sludge

Other Solid Catalysts

- o Hydrocracking
- o Polymerization
- o Hydrotreating and Hydrotreating
- o Merox

HF Alkylation

- o Spent Caustic
- o Spent Bauxite
- o Acid Soluble Oil and Tars
- o Alkylation Sludge

Coking

- o Coke Fines and Scrubber Sludges
- o Purge Coke

Product Treating

- o Liquid Merox
- o Caustics - Phenolic and Sulfidic
- o Doctor

DeSalter Cleanout Sludge

Treating Clays

- o Lube Oils
- o Pyrotol
- o Jet Fuel

Tail Gas Treating

- o Spent Stretford

(a) List Distributed by OSW on February 29, 1984

Once the EPA study is completed, it is likely that additional regulations will be proposed to further control the disposal of refinery wastes.

At a very minimum, all petroleum refineries will have to reevaluate the information developed for their RCRA Part E permit application. This will probably result in a new costly sampling and analysis program and cause long delays in obtaining the permit.

A recently published draft manual (5) on Land Treatment Demonstrations required by 40 CFR 270 indicates that a land treatment demonstration will be lengthy and costly to refiners.

The fact that more waste streams may be controlled by RCRA, the problems with getting a land treatment Part B permit and by the fact that the 1984 RCRA amendments (2) specifies that certain wastes be prohibited from land disposal in the future and that generators must submit reports every two years that describe the quantities, nature and disposition of the hazardous wastes generated, the efforts undertaken to reduce the volume

and toxicity of wastes, and the changes in volume and toxicity achieved from the previous years make it imperative that petroleum refiners and researchers continue their efforts to reduce the toxicity and volume of wastes.

Considerable research and development have been conducted in waste solidification. Solidification can minimize the amount of liquid present and assist in reducing the leachate problem. However, this method does not reduce the volume of waste. It may make the waste non-hazardous but may even increase the volume of waste to be disposed.

Incineration has been in use for certain wastes but some wastes have not been successfully incinerated because of equipment problems. Most incinerators used in the U.S. are designed to incinerate only liquids; however, rotary kiln technology has been used successfully in Europe for several years and may be a potential partial solution to disposing of refinery wastes. Recent research with circulating bed incinerators (6) indicates potential.

In conclusion, new regulations and industry's desire to dispose of wastes in a cost-effective and environmentally safe manner pose some interesting challenges for the next several years and will require some dedicated research and development.

ACKNOWLEDGEMENTS

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ULTIMATE CONTAINMENT OF RESIDUAL HAZARDOUS WASTE IN SALT FORMATIONS

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ABSTRACT

The major theme of hazardous waste management today emphasizes the rendering of hazardous waste into its neutralized or detoxified components through a variety of treatment techniques. The efficiency of the available hazardous waste treatment processes, including incineration, biodegradation, chemical and physical alteration, are less than perfect within economically acceptable limits. The residual, non-reducible hazardous constituents of the treated hazardous waste must be prevented from entering the biosphere.

The permanent isolation of these residual, non-reducible hazardous waste constituents can be accomplished by encapsulation in a matrix within a cavern or vault constructed in salt formations. The ability to design and construct repositories in domal or layered salt formations is an established practice and is not extensively treated in this presentation. This paper summarizes the concept of combining the proven technologies of both cavern (repository) development by dissolution and waste solidification. Beyond the theoretical advantages of this isolation technique, the paper reports on in-situ experiments, conducted within the international hazardous waste community. Actual projects in hazardous waste disposal in salt and closely related programs are also discussed.

INTRODUCTION AND PURPOSE

The recent environmental disasters at Love Canal and Times Beach served to focus public awareness upon the issues of hazardous waste management. Consequently our elected officials undertook the revitalization of the environmental laws by the enactment of the 1984 Hazardous and Solid Waste Amendments to the Resource Conservation and Recovery Act of 1976 (RCRA). The Act now mandates the elimination or reduction of hazardous waste by refining production processes and the recycling of wastes. In those instances where the generation of hazardous waste cannot be avoided, the hazardous constituents are to be detoxified, neutralized or rendered nonhazardous by treatment prior to disposal.

Although the goals and objectives of this new legislation are to be applauded, RCRA does not provide for the disposition of the hazardous constituents of waste (like heavy metals) which cannot be rendered less hazardous by treatment. Clearly these non-reducible hazardous residuals must be managed in order to protect human health and the environment. Placement of hazardous materials in surface impoundments or landfill facilities is unacceptable and is prohibited under RCRA.

The problems associated with the ultimate disposal of these hazardous residuals very closely parallels the difficulties of disposing of untreatable and indestructible radioactive waste. Based upon the best scientific and engineering advice, the Congress identified the containment of radioactive waste in underground repositories, constructed in geologically secure formations, as being protective of human health and the environment, when they enacted the Nuclear Waste Policy Act of 1982 (NWPA).

The ultimate disposal of the residual constituents of hazardous waste by isolating them from mankind and the environment in subterranean repositories constructed in salt formations is environmentally desirable, technically feasible and economically sound. Public confidence, based upon an understanding of the integrity afforded by a system of natural salt barriers, is the sole missing ingredient to the solution of the ultimate disposal problem for residual hazardous wastes.

APPROACH

Why Salt Is A Suitable Environment

Salt, known as sodium chloride or as the mineral halite, possesses several characteristics that qualify it as a prime candidate for a hazardous waste storage medium. First, salt in its native state is solid and very low in permeability (the ability to transmit fluid). This point is often overlooked due to the fact that most of us only see salt after it has been crushed into the granular form we sprinkle on food. Salt is so low in permeability that for all practical purposes it can be considered impermeable. This is a critical factor because the disposal formation must be able to retain the waste, and also, must not permit external water to enter and migrate through the waste.

A second favorable characteristic of salt is its tendency to creep under rock pressure. Voids occurring between the cavern walls and the hazardous waste mass placed in salt will be minimized or closed due to this behavior. This visco-plastic material behavior also contributes to the low permeability of salt by preventing fractures in undisturbed salt rock.

Additionally, salt is strong enough to withstand stresses experienced around a sub-surface excavation, remaining fractureless to a great extent (without any lining) because of its favorable mechanical behavior. The compressive strength of salt exceeds that of concrete commonly used in construction.

Many are aware that salt dissolves when exposed to water and fear the salt formation will dissolve and expose the hazardous waste. As mentioned earlier, salt is impermeable and will not permit the passage of water. Water meeting the exterior surface of a large salt formation will dissolve the outer edge slightly, but will stop as soon as the water becomes saturated with salt. Placing the hazardous waste deep in the salt formation will shield it from exposure by any such dissolution. The fact that most salt formations have been in place for over 200 million years indicates that no major water source has been in contact with the salt.

Disposal in salt also provides the cost saving ability to store mixtures of waste rather than segregated ones. As long as the mixtures of waste are chemically compatible, they can be placed in salt caverns without being submitted to expensive segregation and separate disposal methods. There are a few compounds that must be excluded because they react with sodium chloride, but the majority can be safely deposited in salt. In fact, only a few compounds, such as those containing lithium or bromine trifluoride, cannot be disposed of in salt (1).

Another attractive feature of salt is the fact that salt deposits are located all over the world, generally in areas of low tectonic activity (which means little or no chance of earthquakes). Figure 1 illustrates the location of major salt deposits in the United States.(2) As a rule, the deposits are also massive in size.

Bedded salt formations were deposited in layers that can be several hundred feet thick. These layers are usually separated by relatively thin deposits of shale, a rock that also has very low permeability. Bedded salt can be found throughout the world.

Domal salt deposits are extremely massive in size. An average Gulf Coast salt dome, for example, is several thousand feet thick and underlies a surface area of a couple of thousand acres. Salt domes can be found in many parts of the world, but are not as widespread as bedded deposits.

Salt deposits range in age from 2 million to 600 million years old, with the average being about 200 million years in age.

Finally, an important economic advantage of salt as a safe environment for the disposal of waste is its high solubility in water. As explained in the next section, subsurface space can be created by above ground controlled dissolving or leaching without requiring mining equipment or personnel working in the subsurface.

Construction Of A Cavity In Salt

The alternative to conventional mining - sinking mine shafts into the salt formation and excavating galleries by subsurface drill and blast techniques - is solution mining. This method takes advantage of some of the physical characteristics of the salt. It involves the injection, via a drilled well, of fresh water into a salt formation. The water dissolves or "leaches", the salt. This salt water, or brine, is removed from the cavern by displacement through the same drilled well. The simultaneous water injection and brine withdrawal is accomplished by using two suspended strings of tubing installed concentrically to one another and to the cemented casing (Figure 2).

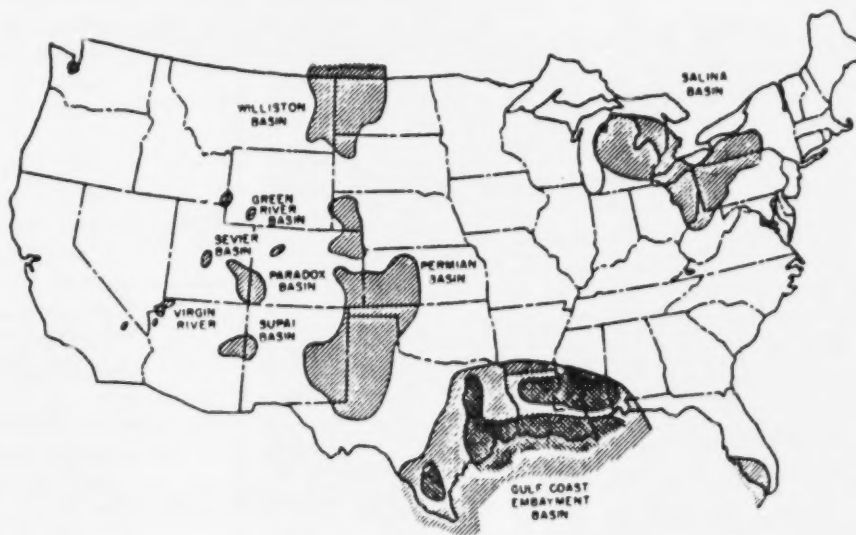


Figure 1: Location of major salt deposits in the United States

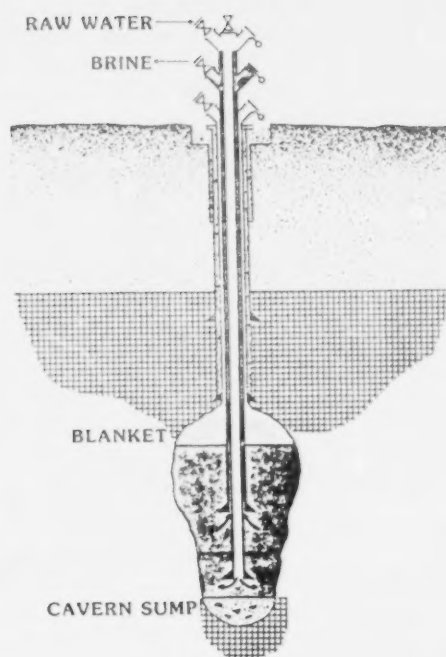


Figure 2. Solution Mining Process
(Schematics)

As seen in Figure 2, the two suspended strings provide three avenues for flow into, or out of, the cavern. The bottom two openings are used for water injection and brine production purposes. The water can be injected into the upper opening and the brine can be withdrawn from the lower of the two, or vice versa, depending on what cavern shape is desired. Cavern shape is also affected by the depths at which these two openings are located.

Further control of cavern shape is attained by injecting a protective medium (blanket) into the cavern via the third, or uppermost, opening. The result is an engineered cavern that can be classified as a permanent structure. An illustration of a typical Strategic Petroleum Reserve (SPR) oil storage cavern is shown in Figure 3.

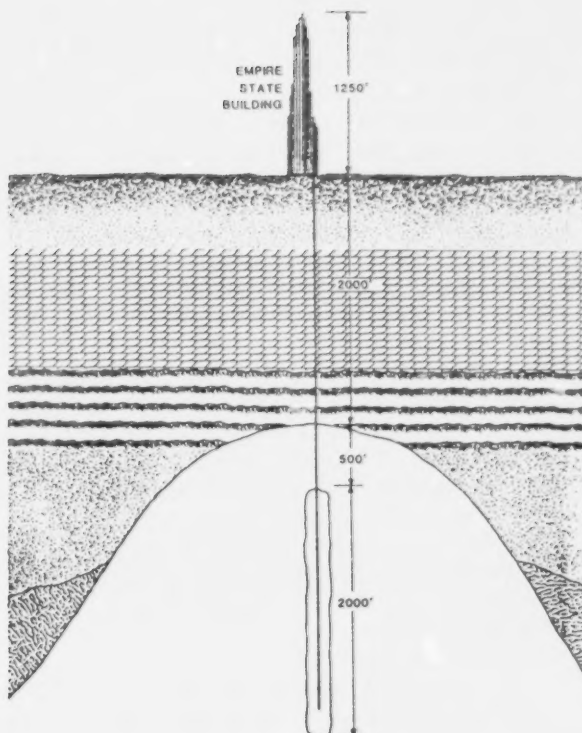


Figure 3. Typical SPR Oil Storage Cavern
In a Gulf Coast Salt Dome
(Cavern Volume = 11 million barrels)

The access well will typically penetrate water bearing formations. During drilling, the well will be completed with several concentric casings that are cemented up to the surface. Each casing string will be pressure tested after it is installed to insure absolute tightness. The well is much smaller in diameter than a mine shaft, and only one well is required instead of the two or three shafts that would be necessary in a conventional mine. Therefore, avenues for connection of groundwater with the well (and repository) are more easily and reliably avoided.

Subsurface Disposal Of Waste

Waste disposal in salt mines has been performed at two locations in West Germany. They are the Asse salt mine, which was used for radioactive waste disposal for many years, and the Untertage-Deponie (subsurface repository) Herfa-Neurode, which has been in successful operation for disposing of chemical waste since 1970.(3).

Although waste disposal in leached caverns has only been investigated using pilot plants, there are several reasons why this alternative is becoming more and more attractive. The basic idea is to process the waste on the surface in such a way that it can be transported through the wellbore into the cavern where it settles until the storage space is totally filled. In the final step, the well will be plugged, thus preventing any further contact between the waste and the environment. No further operations or controls are necessary.

There are several advantages to using solution mined caverns instead of conventional mines for hazardous waste disposal. First, no personnel or equipment are required underground except for the steel tubing that provides access to the cavern. Secondly, access to the waste through the single bore and tubing is very limited, and therefore safer, than the multiple and larger shafts required for a mine. Additionally, the construction cost is much less for a solution mined cavern.

The "wet" and the "dry" deposition methods are two basic ways of operating a waste cavern. In wet deposition, waste is transferred directly into the brine, which is still in the cavern from the leaching process. By injecting waste, the brine will be displaced to the surface and then withdrawn. This method is simple, but the risk of polluting the brine because of the contact with the waste makes this process an undesirable one. The alternative solution, dry deposition, requires the withdrawal of brine prior to disposal of waste, a process which has been proven in practice.

There are two basic types of operations for transferring waste into the cavern. The batch method, where individual cannisters are lowered into the cavern via a wireline, is very time consuming and labor intensive. The preferred type of operation is the continuous method where the waste can be pumped or dropped continuously into the well (Figure 4).

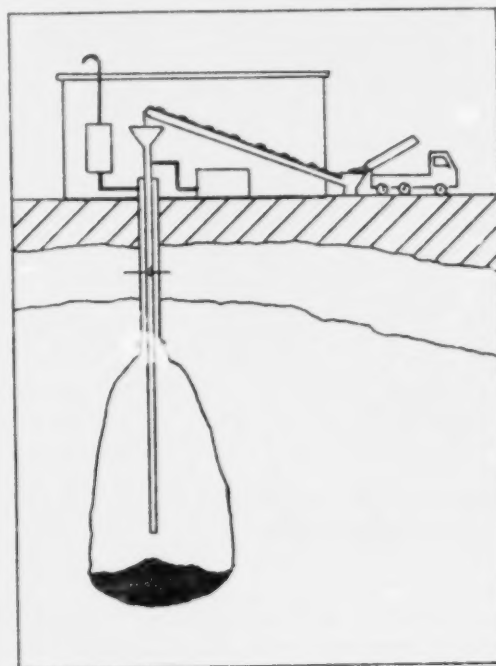


Figure 4. Concept of Continuous Waste Disposal into a Cavern

When using the continuous method, two different approaches are available at present. Both involve solidification of the waste. The first requires solidification of the waste into pelletized form on the surface, or pelletizing waste which is delivered as solids, followed by dropping the pellets down the tubing into the cavern. This results in a tightly packed pile of pellets, although there will remain a certain amount of open pore space between pellets. The second approach involves mixing the waste with a solidification agent and while the mixture is in

slurry form, pumping it into the cavern. The slurry composition can be designed to control the time of solidification in such a way that a massive, continuously growing block will be created in the cavern. In either case, the material will not flow directly through the cemented casing. It will, instead, flow through a hanging string of tubing (inside the cemented casing) because this string can be replaced if any problems such as plugging occur.

Theoretical investigations have demonstrated that deposition of liquid waste without solidification appears to be possible.(4) However, there are several reasons why solid or solidified waste is preferred. First, the mechanical properties of solid waste are more favorable than liquid waste. This is because the mobility of solids is much lower, thus eliminating the possibility of waste "squeezing" out through leaks. Solidification also immobilizes the hazardous components, which minimizes the possibility of reactions between the different chemicals. Additionally, surface area of the waste is minimized, which reduces the amount of toxic constituents that could possibly come in contact with the environment.

With the increasing needs for safe handling of radioactive and chemical wastes, solidification technology is being developed and refined. There are several types of solidification processes which may be considered in the case of hazardous or toxic chemical waste.(5) Two of the more prevalent processes are:

1. **Cement Based Processes.** These use well-known technology and inexpensive and plentiful raw materials and are tolerant to most chemical variations. However, relatively large amounts of cement are required which reduces the net waste volume.
2. **Pozzolanic Processes.** These require using lime or lime substitutes and pozzolana to produce a solidified product. A typical pozzolana is flyash. Materials are often very low in cost and widely available, with little special equipment needed and relatively well-known reactions.

Each of these processes have inherent advantages and disadvantages. Decisions as to use will have to be based on the chemical and physical properties of the specific waste.

Repository Closure

After the final lift or course of hazardous residual material has been placed and taken its initial set, a cap of structural quality concrete is placed. The concrete cap completely fills the void between the solidified material and the arched roof of the cavern but does not extend up into the throat of the uncased borehole. The uncased borehole, extending up from the throat of the cavern to the casing shot, is packed with a mixture of sodium chloride, potassium chloride and calcium sulphate salts, lubricated by a saturated brine solution. The lithostatic pressure, generated by the salt rock, will cause recrystallization of these salts, forming a solid plug. This plug, which defies identification other than by chemical analysis, effectively seals off the cavern and its contents. The cased borehole above the recrystallized plug is cemented back to the surface by conventional well abandonment procedures. The benefit of this closure technique is to achieve the Macroencapsulation of the solidified hazardous residuals with native materials thus avoiding the possible failure of manmade, engineered components.

Post Closure Monitoring

The long term efficiency of the containment and isolation system will be monitored over a minimum period of 30 years after closure. During the site characterization process, performed during the permitting process, environmental data is accumulated and assembled into an environmental background model. Water samples from peripheral monitoring wells will be analyzed to detect chemical changes in the groundwater. The absence of change in the profile validates the integrity of the repository.

During placement of the hazardous residuals, minute quantities of tracer isotopes are added to imprint the specific hazardous residuals with a unique signature. If, during the monitoring process, there is a shift away from the baseline profile, and the trace signature is absent, the change must be attributed to causes other than migration from the repository.

PROBLEMS ENCOUNTERED

Technical Design

As described, the technologies for the individual components of a hazardous waste repository in salt exist. However, the application and combination of these elements to the needs of a hazardous waste repository will require some additional research and development. This is true, in particular, in the selection of the most suitable waste materials, the solidification process and the slurry transport.

Regulatory Regime

RCRA mandates implementation of its regulations by the Environmental Protection Agency (EPA). The Act is not passive, it establishes technical goals for the Agency, requires rule making and the development of enforcement procedures within very specific and inflexible time tables. The regulatory and administrative burden on EPA is substantial. The impact on the regulated community is devastating. For example, section 3004(b) of RCRA prohibits the placement of hazardous waste in salt formations until the Administrator (EPA) promulgates specific rules. The EPA suggests that under its mandated rulemaking schedule it may take as long as 42 months before these rules are published. Can we really wait that long before addressing the ultimate containment issue?

Public Education

The public is aroused about the dangers of health threatening leachate migrating from surface impoundments and landfills into aquifers designated as underground sources of drinking water. This well founded fear is based upon the common knowledge that water can migrate or percolate through soil. Intuitively, the concept of water movement through underground formations leads to the erroneous conclusion that salt formations can be attacked by water and that the salt will be "dissolved away".

A public education program designed to help the people living in the proximity of a proposed containment repository appreciate the integrity of a salt dome that has withstood the ravages of 200 million years of evolutionary geology without being "dissolved away" is a self evident need that must be met.

Everyone is in favor of cleaning up existing leaking surface impoundments and landfills. Everyone is in favor of constructing effective hazardous waste management facilities; - but "NIMBY", which translates into "not in my back yard". The NIMBY syndrome is so deeply rooted that even state governments have enacted legislation outlawing the construction of hazardous waste treatment and disposal facilities within their state.

Clearly the most significant problem faced by those involved in the effective management of hazardous waste is the presentation of accurate and timely information to the public in an understandable and believable manner. Public trust can only come from an informed citizenry and neither the regulators or the regulated community have been effective in this critical area.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

RESULTS

General Experience

For over 30 years, solution mined caverns in salt formations have been used for storage of hydrocarbon liquids and gases. They have been located in both bedded and domal salt deposits and operated by oil and gas companies, pipeline companies and various other energy-related organizations. Since 1978, the Department of Energy's (DOE) SPR Program has been creating and filling salt caverns with crude oil to maintain a reserve in case of national emergency. At the time of this writing, more than 380 million barrels of crude oil are in storage in solution mined caverns created in salt domes in Louisiana and Texas. All of this crude oil, considered a hazardous liquid if spilled, is being safely contained under pressure without threatening the environment.

In 1965, the Atomic Energy Commission (AEC), with the assistance of Oak Ridge Laboratories, deposited high level nuclear fuel rods in the Carey salt mine in Lyons, Kansas. The principal objective of this experiment, called project Salt Vault, was to demonstrate both the feasibility and safety of the disposal of solidified high-level radioactive wastes in salt cavities. This included demonstration of techniques and equipment which might be used in an actual disposal facility as well as the collection of data on the properties and behavior of in-situ salt subjected to this radioactive material. The project was a success in all of these areas during its two years of operation.

At present, the Waste Isolation Pilot Plant (WIPP) is under construction near Carlsbad, New Mexico. It is a research and development facility to demonstrate the safe disposal in salt of radioactive wastes from the United States defense programs.(6) Mine shafts have been sunk and enlarged; extensive excavation of rooms in the salt has been completed and detailed data gathering and testing has been accomplished. The next step is an actual test of nuclear waste disposal on a small scale in the salt. Barring unforeseen complications or problems, the WIPP could be ready for receipt of radwaste on a full-scale basis within two or three years.

In West Germany, the Asse II salt mine was acquired by the government-owned company GSF (Gesellschaft fuer Strahlen und Umweltforschung) in 1965 for the purpose of conducting research and development work for the disposal of radioactive waste in salt. From 1968 to 1978, 125,000 barrels of low level and 1,200 barrels of medium level radioactive waste were disposed in this mine. The experience gained from this full-scale plant is one of the bases for the design and future operation of the official West German radioactive waste disposal facility at Gorleben, which is now under construction.

Three investigative programs performed in the Asse II mine are of particular importance for the design of a hazardous waste disposal facility in salt caverns, as they are directly applicable.

1. To investigate the rock mechanical stability and the volume closure of a deep cavern under atmospheric pressure, a 63,000 bbl cavern was mined and intensively investigated over a period of 7 years. It was demonstrated that even at the depth of 3200', no stability problems occurred. The percent volume losses due to creep stabilized at 0.4% per year.(7)
2. Kavernen Bau-und Betriebsgesellschaft mbH, German parent company of PB-KBB Inc., leached 5 model caverns within the mine. These excavations were filled with a representative mixture of cement slurry and dummy pellets. During this experiment the hydration temperature in the settling cement, the spreading behavior and the mechanical properties of the solid mass were investigated intensively. (8)
3. At the present time, a demonstration plant for testing long distance slurry pumping is under operation. A pipeline was installed from the surface to the 3150' level. A total of 6300 bbl of cement slurry is to be pumped into the mine at a design flow rate of 30 bph. The aim is to investigate long-term safe pump operation and the mechanical quality of the solidified cement.

In regard to operating a chemical waste disposal facility in salt, there is one known subsurface repository at Herfa-Neurode in West Germany. This full-scale plant in an abandoned potassium mine is commercially operated by the firm Kali+Salz. Since 1970, when this mine was converted to a hazardous waste repository, more than 400,000 tons of waste have been dumped at a depth of about 2300'. The waste is delivered to the site by truck in barrels on one-way pallets. Each kind of waste must first be accepted by the operator and the supervising authority. Liquid waste will be stored only after solidification.

In the comprehensive article in National Geographic "Storing Up Trouble...Hazardous Waste", this plant was mentioned as the most impressive solution to the hazardous waste disposal problem.(9)

CONCLUSION

The elements of a balanced four part program to eliminate the hazardous waste problem are:

1. Elimination of, or the reduction in quantity of, the hazardous wastes generated;
2. Rendering of the unavoidably generated hazardous wastes nonhazardous by appropriate treatment technologies;
3. Disposal of the treated, nonhazardous constituents in regulated landfill facilities;
4. Ultimate containment and isolation of the indestructible and untreatable solidified hazardous residual constituents in repositories constructed in geologically stable salt formations.

The required technological tools are at hand, the legislative intent has been enacted and the regulatory mechanism is being developed. Significant progress in the management of hazardous waste is imminent.

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LABORATORY AND PILOT PLANT ASSESSMENT OF THE
ACID PRODUCTION POTENTIAL OF MINING WASTE MATERIALS

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ABSTRACT

The role of the microorganism Thiobacillus ferrooxidans in the oxidation of sulphide minerals and the production of acidic effluents from mining wastes is discussed and the chemistry involved explained. T. ferrooxidans plays an important role in acid production due to its ability to rapidly oxidize reduced sulphur and iron which, when sulphides are present, and result in the generation of sulphuric acid. The sulphide mineral pyrite (FeS_2), often present in mine waste materials, is generally recognized as the chief source of acid mine drainage.

A small-scale test procedure is explained which rapidly evaluates the inherent capability of a waste material to produce an acidic effluent. If the waste material is assessed as a potential acid producer, then scale-up testing procedures are available which can be used to simulate the characteristics of the effluents produced from a commercial sized waste dump.

During periods of little rainfall, localized biological activity may occur in wet areas of a dump, resulting in the possible accumulation of water soluble pollutants. The length of these dry periods greatly affects effluent loadings and characteristics during subsequent rainfalls.

Acid-base accounting can be used to identify where the acid producing and acid consuming materials are located in an orebody. The data produced from tests on core samples, composited over suitable short intervals from multiple drill holes, can provide an excellent overview of the distribution and placement of both alkaline and sulphidic materials.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

AN OVERVIEW OF PILOT-SCALE RESEARCH IN HAZARDOUS WASTE THERMAL DESTRUCTION

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ABSTRACT

The enactment of the Resource Conservation and Recovery Act (RCRA) of 1976, Toxic Substances Control Act (TSCA) of 1976 and Superfund legislation of 1980 has intensified research in the area of hazardous waste thermal destruction. As a result, a large amount of useful information has been accumulated. This paper summarizes and compares ongoing pilot-scale studies being conducted in this area ranging from oxidation to pyrolytic thermal destruction, and from conventional to innovative processes. This paper provides:

- Information summarizing the thermal destruction testing results for selected waste compounds.
- Recommendations regarding future directions in the area of hazardous/toxic waste thermal destruction research.

INTRODUCTION

Unsound disposal of organic hazardous/toxic wastes has been posing a serious threat to human health and the environment. The Federal government responded to the critical hazardous waste problem with the enactment of the Resource Conservation and Recovery Act (RCRA) in 1976 (Public Law 94-580), Toxic Substances Control Act (TSCA) in 1976 (Public Law 94-469), and a comprehensive "Superfund" program in 1980 (Public Law 96-510) to assure the reliable management of hazardous/toxic waste disposal operations and dump site clean-up. The enactment of these Laws has intensified

research into the thermal destruction of organic chemical waste and the research has accumulated a large amount of useful information. This paper describes some of the past and current efforts in the area of pilot-scale research that has come about due to the passage of RCRA and TSCA. The purpose of this paper is to provide information relative to "who is doing what" for the hazardous waste management industry in terms of generating research information and relative to planning future programs. This paper covers the following research activities:

1. EPA's Combustion Research Facility (CRF) at Pine Bluff, Arkansas
2. EPA's Destruction of Hazardous Wastes Cofired in Industrial Boilers
3. EPA's Mobile Incinerator at Edison, New Jersey
4. EPA's Controlled Temperature Tower at Cincinnati, Ohio
5. EPA's Rotary Kiln Incinerator Simulation at Research Triangle Park, N.C.
6. Fundamental Flame Combustion Research Program at Union Carbide
7. EPA's/New York State's Destruction of Hazardous Waste Using Plasma Arc Technology
8. Destruction of Hazardous Waste Using Huber's Advanced Electric Reactor

PILOT-SCALE RESEARCH OF HAZARDOUS WASTE THERMAL DESTRUCTION

1. EPA's Combustion Research Facility (CRF) at Pine Bluff, Arkansas⁴

Research Scope

- To develop methods of improving the reliability and controllability of the incineration processes.
- To understand the hazardous waste incineration processes and to assist in the development of methods to predict the performance of incinerators.
- To support RCRA incinerator regulations and performance standards, and to provide additional technical basis for those future stand-

ards which may be necessary.

Research Approach

The CRF, located at the site of the National Center for Toxicological Research, Pine Bluff, Arkansas, houses a rotary kiln (construction completed in July 1984) and a liquid injection incinerator (currently under construction). Major characteristics of the rotary kiln include:

- A rotary kiln incinerator (8' length x 4' diameter, 1.8MMBtu/hr) and an afterburner (10' length x 3' diameter, 1.8MMBtu/hr).
- Primary fuel for both the kiln and afterburner is propane.
- Scrubber and air pollution control devices (3800 ACFM capacity).
- Sampling systems and analytical instruments are comprised of two gas chromatographs (GCs) with Autosamplers, a high pressure liquid chromatograph (HPLC), and associated sample preparation equipment. Hot-zone sampling is available in both the kiln and the afterburner transfer ducts to complement sampling of stack gases. Real-time monitoring of O₂, CO and CO₂ levels is provided by an automated system. EPA Method 5, Modified Method 5 (using cooled XAD-2 resin collection medium), and the volatile organic sampling train (VOST) system for relatively low-boiling organics are routinely used.

Research Status

Hexachlorobenzene (HCB) and 1,2, 4-trichlorobenzene (1,2,4-TCB) have been used as surrogate Principal Organic Hazardous Constitu-

ents (POHCs) to test the performance of the rotary kiln during 34 test burns. These two compounds were tested as POHCs because they are recognized as thermally stable compounds, widely found in certain categories of industrial hazardous wastes, and suspected of being precursors in the formation at elevated temperatures of potentially significant products of incomplete combustion (PICs).

Testing

Measurement results are compared to combustion stoichiometry which can be depicted as follows:

- (A) Propane Combustion:

$$\text{C}_3\text{H}_8 + 5\text{O}_2 \longrightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$$
- (B) Toluene Combustion:

$$\text{C}_7\text{H}_8 + 9\text{O}_2 \longrightarrow 7\text{CO}_2 + 4\text{H}_2\text{O}$$
- (C) TCB Combustion:

$$\text{C}_6\text{H}_3\text{Cl}_3 + 6\text{O}_2 \longrightarrow 6\text{CO}_2 + 3\text{HCl}$$
- (D) HCB Combustion:

$$\text{C}_6\text{Cl}_6 + \frac{9}{2}\text{O}_2 + 3\text{H}_2\text{O} \longrightarrow 6\text{CO}_2 + 6\text{HCl}$$
- (E) $2\text{HCl} + \frac{1}{2}\text{O}_2 \longrightarrow \text{Cl}_2 + \text{H}_2\text{O}$
- (F) $\text{Cl}_2 \longrightarrow 2\text{Cl}^{\bullet}$

Findings and conclusions of the 34 test burns are summarized below:

- The CRF rotary kiln system can consistently produce Destruction and Removal Efficiency (DRE) values above 99.99% for refractory POHCs (HCB and 1,2,4-TCB).
- DRE values below 99.99% were obtained during several types of failure mode simulations (flameout in kiln or afterburner).
- The feed of HCB or 1,2,4-TCB in toluene produced a large number of PICs, notably polycyclic aromatic

hydrocarbons (PAH) and other chlorinated benzenes. The PICs were tentatively identified by GC methods and confirmed by GC/MS. A number of these compounds are toxic or possibly carcinogenic. No dioxins or dibenzofurans were identified in any of the analyses for PICs. Examples of PICs at the ppm to ppb concentration level identified from the HCB and 1,2,4-TCB burns are:

- 1,3-dichlorobenzene
 - 1,2,4-trichlorobenzene
 - hexachloroethane
 - 1,2,4,5-tetrachlorobenzene
 - benzyl chloride
 - pentachlorobenzene
 - hexachloro-1,3-butadiene
 - hexachlorobenzene
- After a test burn with either HCB or 1,2,4-TCB in the feed, significant amounts of the POHC were found to be emitted during subsequent tests wherein the only feed to the kiln was propane fuel.
 - Analytical data from hot zone samples show that the concentrations of organic compounds found did not correlate with particulate levels, which supports the assertion that the organic molecules are in the vapor state (not strongly associated with particulates) in the hot zones.
 - Deliberate reduction of excess air levels resulted in significant production of soot and PICs but did not produce higher levels of CO in the combustion gases.
 - Complex chemical interactions occur in the afterburner. In the case of HCB as the POHC, for example, previously formed intermediate combustion products may react

to form additional HCB in the afterburner. Under some conditions, POHC output from the afterburner was greater than the POHC input to the afterburner. This could result from reactions between intermediate products, hold-up from previous burns, or a combination of these effects.

- There was no apparent effect of residence time/temperature or feed rate on DRE over the ranges covered in the test series.
- DRE values for 1,2,4-TCB were higher than for HCB under comparable residence time/temperature conditions.
- Most of the thermal destruction occurred in the kiln.
- There is apparently a direct relationship between the DE (Destruction Efficiency) of the afterburner (DE_{AB}) and the POHC injection rate at very low injection rates. The behavior of the DE_{AB} at very low injection rates appears to result from a combination of POHC/ PIC carry-over (holdup) from previous burns plus PIC formation in the afterburner.

2. EPA's Destruction of Hazardous Wastes Cofired in Industrial Boilers

Research Scope

- To gather data to aid the EPA in selecting a strategy or set of strategies for regulating the combustion of hazardous wastes in boilers.
- To identify which of several boiler operating parameters have a major impact on boiler destruc-

tion and removal efficiency.

- To evaluate and, if practical, establish a mathematical model for predicting an upper limit on the amount of cofired waste that could be charged. In particular, those parameters that could be easily changed by an operator or might represent major differences between boiler types were studied.
- To gain sufficient information to allow judgments regarding what particular parameters are useful in comparing pilot-scale with full-scale boilers.
- To obtain information that would give insight on how regulations might be cast so that trial burns would not be needed.

Research Approach

- Under a contract to EPA, the Acurex Corporation conducted this study and carried out testing at Acurex's site in Mountain View, California.
- The pilot-scale furnace tested was a packaged D-type water boiler and had a rated capacity of about 1.5 million (MM) Btu/hr.
- A detailed characterization of the thermal history and environment of the furnace under various sets of operating conditions was carried out.
- A study of the DRE of one compound as conditions were varied was conducted.
- A study of the DRE's of several compounds burned simultaneously (a composite "soup") was performed.

- Parameters studied included excess air rate, fuel firing rate, amount of waterwall surface area, swirl setting and waste type.
- Chlorobenzene was used for the single compound. For the multiple compound tests, chlorobenzene was fired with carbon tetrachloride, chloroform, methylene chloride, and dichloroethane.

Testing

All tests were performed in the Acurex Pilot-Scale Furnace. The furnace has a single burner, front wall fired, into a horizontally oriented firebox. The premixed fuel oil/waste mixture is pumped out of drums through a pressure-atomizing nozzle and stabilized at the front wall. The fuel flow is monitored by rotameter. Combustion air is preheated and injected in the annular region around the fuel delivery tube. The International Flame Research Foundation (IFRF)/ Acurex burner design allows swirl adjustment by rotating swirl blocks. Air flow is monitored by hot wire anemometer.

In general, a test is divided into four stages: fuel preparation, furnace heatup, sampling, and analysis. Fuel was prepared by mixing known volumes of waste and distillate oil in clean 55-gal drums. Furnace heatup could occur either from a cold start or a hot start, and involved bringing the furnace walls to a preset temperature (below the expected run temperature) with natural gas firing and then switching to the test fuel until the temperature reached the final run temperature. This heating phase could take from 4 to 16 hr. Sampling was done for the temperature readings and gas sample locations specified for the program. Analysis encompassed both the prerun

preparation and QC of sampling trains and collected media as well as post-run analysis of the collected samples.

Test series A, the baseline studies, consisted of seven runs, all with no waterwalls present. Three swirl settings, two nominal firing rates, and three nominal stoichiometries were considered. Baseline conditions (no waste in the fuel) were not repeated with waterwalls because it was found to be unnecessary. Thus work could immediately start on DRE studies. Test series B, the single compound tests consisted of ten runs, seven without waterwalls and three with waterwalls. Two nominal firing rates, three stoichiometries, and two swirl settings were studied. Test series C, the multiple compound tests, included 32 runs, all with waterwalls present in the firebox.

Study Conclusion

Of the variables studied, the order of influence on DRE is: waterwalls > compound > excess air > firing rate > flame shape. The order of influence on temperature profiles is: waterwall > excess air > firing rate > compound $\approx$ flame shape. Except for waste composition, the influence of operational variables on DRE corresponds to the influence of temperature. From comparison of DRE with and without waterwalls it is concluded that in-flame destruction accounts for only about 90 to 99 percent of the DRE. The remaining destruction must be achieved from postflame thermal oxidation and decomposition.

Residence time within flame is insufficient to destroy both POHC's and PIC's. Without sufficient post-flame time and temperature, the quantity of PIC's passing out of the boiler will be significant.

Significant VOC (Volatile Organic Compound) PIC's emitted during combustion of chlorinated organics include methylene chloride, ethylene trichloride, perchloroethylene, and the ethylene dichlorides. Suspected VOC PIC's but not positively identified include chloromethane, chloroethane, chloroethylene, and propylene chloride. The testing also showed that although DRE's for both POHC's (chlorobenzene and carbon tetrachloride) are greater than 99.99 percent, the DRE of total chlorinated organics as fired is only 99.985 percent.

A model capable of predicting within a few degrees the temperature profile within a furnace has been validated. The model can be used to predict within an order of magnitude the destruction efficiency of the modeled furnace.

Trial Burns

The key test materials and purposes are as follows:

TRIAL BURN TEST SUMMARY

Test No.	Feed Material	Number of Runs	Test Purpose
1	Diesel Fuel	2 DRE ^a 2 Particulate ^b	Baseline performance.
2	1.2% Fe ₂ O ₃ ^c 98.8% Diesel fuel	3 Particulate	Particulate removal efficiency of APC.
3	21.4% CCl ₄ ^d 28.9% C ₆ H ₄ Cl ₂ ^e 49.7% Diesel fuel	3 DRE 3 Particulate	Destruction of RCRA organic; HCl removal efficiency of APC.
4	11.4% Askarel ^f 88.6% Diesel fuel	3 DRE 3 Particulate	Destruction of PCB (TSCA); HCl removal efficiency of APC.
5	39.3% Askarel ^f 60.7% Diesel fuel	3 DRE 3 Particulate	Destruction of PCB; HCl removal efficiency

a - Destruction and removal efficiency of principal organics.

b - NJDEP Incineration Test Method

c - Iron oxide.

d - Carbon tetrachloride or tetrachloromethane

e - Ortho-dichlorobenzene or 1,2-dichlorobenzene

f - 58.9% Aroclor 1260, 35.0% trichlorobenzenes, 6.1% tetrachlorobenzenes

3. EPA's Mobile Incinerator at Edison, New Jersey^{6,7}

Research Scope

- To provide a mobile facility for on-site thermal destruction/detoxification of hazardous and toxic organic substances.

Research Approach

In 1981, EPA constructed a mobile incinerator system which consists of four heavy duty, over-the-road, semi-trailers. They are:

- Trailer 1: Rotary kiln
- Trailer 2: Secondary combustion chamber
- Trailer 3: Scrubber and air pollution controls (APC)
- Trailer 4: Combustion and stack gas monitoring equipment

Trial Burn Results

The test results from the trial burn cover principal performance criteria: (1) particulate matter removal efficiency, (2) HCl removal efficiency, (3) organic destruction and removal efficiency, (4) wastewater quality, and (5) ambient air quality. The first three criteria are related to stack emissions and are heavily regulated by the RCRA. The requirements specified by RCRA are: (1) maximum allowable particulate matter emission rate of 180 mg/m³ when corrected to 7% oxygen in the stack gas; (2) HCl removal of 99% or a release of 1.8 kg/hr (4 lb/hr) for the stack emission, whichever is greater; and (3) minimum organic DRE (e.g., for tetrachloromethane, trichlorobenzenes, and tetrachlorobenzenes) of 99.99%. During all trial burn tests, the system performance met the requirements for each of these criteria.

The POHCs and their DRE's found during the trial burns were:

<u>POHC</u>	<u>DRE</u>
CCT ₄	>99.99996
C ₆ H ₄ Cl ₂	>99.99998
C ₆ H ₃ Cl ₃	>99.9998
C ₆ H ₂ Cl ₄	>99.9994
Aroclor 1260	>99.9998

The water quality criteria covers the analysis of TOC, pH, temperature, total dissolved solids, total suspended solids, petroleum hydrocarbons, volatile organics, and the test organic compounds. The concentration of the test organics in the wastewater was lower than 20 µg/l (ppb)(i.e., limit of detection) during the entire trial burn. The main contaminants in the wastewater were dissolved salts from the neutralization of acid gases (HCl and

fuel-oil derived SO₂) with scrubbing solution (sodium bicarbonate and carbonate).

The ambient air quality criteria cover air collection and analysis at 0.3 to 1.0km downwind from the incinerator stack. No measurable quantities of chlorobenzenes or PCBs were detected. The detection level for both trichlorobenzene and tetrachlorobenzene was 0.1 µg/m³ and for PCBs (as Aroclor 1260) was 1.0 µg/m³. These data verify the conclusions of an EPA air dispersion modeling evaluation (conducted prior to the trial burn) which indicated that the mobile incinerator would not adversely impact the quality of air in the local community.

As a conclusion, based on the high combustion and destruction efficiencies measured during the trial burn, the EPA Mobile Incineration System has been shown to be an effective implement for the destruction of hazardous organic materials. In fact, the level of combustion and destruction reported was essentially based on analytical limitations of measurement rather than on the actual finding of hazardous components in the stack emissions. The results of the trial burn indicate that the system apparently met or exceeded all applicable federal requirements for incineration systems.

4. EPA's Controlled Temperature Tower at Cincinnati, Ohio

Research Scope

- To establish how combustion parameters and variables affect failure of a simulated hazardous waste incinerator or an industrial boiler that cofires hazardous waste with conventional fuel to achieve 99.99% DRE;

- To determine how, when and why PICs are formed (e.g., too low oxygen concentration or too low an operating temperature) and to determine how or whether they can be subsequently destroyed or removed (e.g., by secondary combustion or scrubbing/ adsorption techniques); and
- To determine which organic chemicals are the hardest to burn (this will assist in making better POHC selections).

Research Approach

To supplement its extramural research, EPA has constructed both pilot- and bench-scale combustors at their Center Hill Facility, part of their Hazardous Waste Engineering Research Laboratory in Cincinnati, Ohio. The largest of these combustors known as the Controlled Temperature Tower (CTT) is very flexible for the simulation of incinerator behavior at the small pilot scale and has the following special features in its reactor chamber:

- In the flame zone, the chamber is refractory-lined. The main flame is typically a swirl-stabilized turbulent spray flame. A variable swirl-block IFRF burner is available that allows testing nominally at 150,000 Btu/hr.
- The second section is equipped with cooling coil access. Thus, the heat extraction rate can be varied by changing the amount of cooling coil surface exposed [ranging from no heat removal to very high removal (to provide extreme thermal quench rates)].
- In the third section, the wall is auxiliary-heated to reduce losses from the furnace gases. The

degree of back-heating provides various thermal profiles in this third section.

- The chamber downstream of the flame can be used to study the impact on DRE and on PIC minimization of the use of secondary combustion techniques.

Research Status

The unit has been installed and is undergoing shakedown testing. Personnel responsible for operating this unit are currently fine-tuning testing protocols, performing QA/QC activities, and readying the unit for longer term operation.

5. EPA's Rotary Kiln Incinerator Simulation at Research Triangle Park (RTP), N.C.

Research Scope

- To determine time/temperature requirements for solids detoxification
- To develop process information
- To predict materials interactions
- To provide detailed information on operational failure modes

Research Approach

A pilot-scale rotary kiln combining with a vertical afterburner was recently installed at the EPA-RTP facility. The unit has the capacity of 350,000 Btu/hr with natural gas as the major fuel and has an afterburner rated at 160,000 Btu/hr. The unit was designed to simulate the function of a full-scale rotary kiln for evaluating various parameters such as:

- A. Parameters of simulation
- Kiln motion and rotation speed
 - Wall temperature
 - Gas temperature
 - Solids time/temperature profile
 - Transient characteristics (feeding effects)

- B. Parameters that affect failure modes

- Overcharging:
 - Aqueous waste
 - Volatile release
- Materials Interaction:
 - Capsulation
 - Insulation
- Short circuiting
 - Insufficient solid phase residence time
- Flame perturbations

- C. Parameters that affect solids de-toxification

- Burning mass thickness and motion
- Wall temperature
- Gas temperature
- Flow field
- Solids residence time
- Gas emissivity
- Load
- Transient characteristics
- Gas composition

The general approach to be used on this project includes:

- A. Establish and validate simulation capability. Compare with full-scale data where available. (Temperatures, times, loading).
- B. Conduct screening experiments to:
- Pose critical questions
 - Identify critical phenomena controlling DRE's
 - Establish pertinent hypotheses
- C. Conduct critical experiments to prove or disprove hypotheses; specific approaches will include:

- Proper selection of solid waste mixtures such as:
 - Solids and semi-solid chemical wastes
 - Contaminated soils
 - Containers: Scaled-down drums containing surrogate hazardous wastes

- Measure DRE versus:
 - Time
 - Size of charge (waste concentration)
 - Performance parameters (THC, CO)
- Analyze for PIC's; determine impact on PIC levels of:
 - Temperature profile
 - Excess O₂

6. Fundamental Flame Combustion Research Program at Union Carbide²

Research Scope

- To develop a better understanding of what is going on in the flame zone when fuel oils of different (chemical and/or physical) properties are burned.
- To maximize the hydrocarbon destruction efficiency and minimize the production of incomplete combustion intermediates.

Research Approach

A research combustor (liquid injection) has been constructed and has been tied in with the existing Union Carbide South Charleston Technical Center waste incinerator. The existing Union Carbide South Charleston Technical Center waste incinerator manufactured by Brule has three combustion chambers. The new combustor has been tied into the bottom of the second existing combustion chamber and shares the third existing combustor.

tion chamber to provide additional residence time and better mixing. The two systems have been connected together with an 18 foot long, refractory-lined, 2 foot ID duct. A cut-off blind has been installed near the new research combustor so that the two systems can be separated completely. The new research combustor will be operated only when the existing waste incinerator is not being used so that the new research combustor will have no impact on the operation of the existing incinerator (and vice versa).

The research combustor was designed for a normal load of three million Btu/hour and a three second residence time. (An additional one second residence time is provided by the 18 foot refractory-lined duct and the up-pass combustion chamber of the existing incinerator.) The maximum load is five million Btu/hr. The normal design operating temperature is 2200°F and the maximum operating temperature is 2500°F.

The system was designed to be able to test different burners, different nozzles and different property fuels. In the initial stage, a research burner developed by the International Flame Research Foundation will be used extensively to study the impact of various air/fuel mixing patterns on the flame zone. Other burners may be studied at a later time. For the first year, only fuel oils (Nos. 2 through 6) will be burned in the research combustor. No actual hazardous wastes under 40 CFR PART 261, Subparts C and D will be tested. After gaining experience with fuel oils, Union Carbide will start the RCRA Part B application process so that research on the combustion of real hazardous wastes can begin.

7. EPA's/New York State's Destruction of Hazardous Waste Using Plasma Arc¹

Research Scope

- To test the limitation of the plasma technology capability to destroy and remove a variety of hazardous wastes.
- To provide data which is necessary to establish conditions of continuous operation, system durability, and costs for maintaining the system.
- To encourage the development and demonstration of innovative technologies for treating and destroying hazardous wastes in a more cost-effective manner or to dispose of the waste which conventional techniques cannot handle.
- To provide a proven method for New York State to dispose of difficult-to-treat wastes.

Research Approach

Under a Cooperative Agreement, the EPA's Hazardous Waste Engineering Research Laboratory in Cincinnati, Ohio and the New York State Department of Environmental Conservation co-sponsor a project to construct and to test a pilot-scale plasma arc technology for hazardous waste destruction. A plasma (which produces temperatures estimated to be as high as 50,000°C) is an ionized gas flow resulting from an electrical discharge. It uses extremely high-intensity energy to break the chemical bonds of hazardous waste molecules down to the atomic state, and their recombination results in simple molecules such as hydrogen, carbon monoxide, carbon and hydrochloric acid in the effluent

gas. The off-gases from the plasma system are scrubbed to remove hydrochloric acid and are then flared.

The implementation of this project involves the following phases of activities:

Phase I. Construction of the mobile pilot-scale plasma arc unit. The capacity of the unit is nominally designed to be four kilograms (8.8 pounds) per minute, and to fit, with ancillary equipment, in a 45-foot trailer. The unit's capacity is around 1.7×10^6 Btu/hr. Construction of this unit has been completed.

Phase II. Testing at Kingston, Canada

Stage 1: Shakedown (completed)

2 kg/minute of ethanol(liquid) was tested for 2 hours. The result was satisfactory. The ethanol was destroyed to the undetectable level.

Stage 2: Individual compound tests, 4kg/minute	% Compound (by weight)
• 3-1 hr. Carbon tetrachloride tests	50
• MEK (methyl ethyl ketone) tests	50
Stage 3: PCB tests, 4kg/minute	
• 3 - 1 hr. Askarel tests	
• 3 - 6 hr. Askarel tests	

Askarel contents: Aroclor 1242 (thick oil)	10
1254	10
1260	10
Chlorobenzene	20
MEK	50

Stage 4: Soup Tests, 4kg/minute

- 3 - 1 hr. soup tests
- 3 - 6 hr. soup tests

Soup contents: Trichloromethane	5
Tetrachloromethane	25
Trichlorophenol	5
Hexachlorohexane	5
Tetrachloroethene	5
Hexachlorocyclopentadiene	5
MEK	50

Phase III: Testing of Critical Waste

If Phase II testing is proven as successful as is currently anticipated, the plasma system would be considered for testing actual waste in New York State at a hazardous waste site.

8. Destruction of Hazardous Waste Using Huber's Advanced Electric Reactor (AER)³

Research Scope

- To perform tests on both a 3-inch (36 pound/hour capacity) and a 12-inch diameter (2,500 pound/hour capacity, 3.4 million Btu/hr) pilot unit constructed by the J.M. Huber Corporation. The purpose of conducting these tests is to determine: (1) the performance of the AER to destroy PCBs, CCl_4 and dioxin mixed with soils; and (2) the suitability of the tested solids for landfill under the Resource Conservation and Recovery Act guidelines. The dioxins tested were Octachlorodibenzo-p-dioxin (OCDD) and 2,3,7,8 Tetrachlorodibenzo-p-dioxin (TCDD).

Research Approach

The AER is an electrically-heated, gravity-fed fluid wall reactor which destroys organics by rapidly heating feed materials to temperatures of 1100°C to 2760°C using intense radiation in the near infrared. Reactants are isolated from the cylindrical reactor core by a gaseous blanket formed by flowing nitrogen radially inward through the proprietary porous core wall. Carbon electrodes, designed to operate reliably at extremely high temperatures, are located in the annulus between

the graphite core and the outer vessel. These electrodes are used to heat the core wall to incandescence. Heat transfer to the feed materials is accomplished predominantly by radiative coupling. Destruction of organics is accomplished by pyrolysis rather than oxidation.

The solid feed is gravity fed from an air-tight feed hopper into the top of the AER. Solids fall through the AER where waste vaporization and pyrolysis occur. For a given reactor length, solids residence time is determined by the balance between the highly viscous, hot nitrogen and gravitational forces. The product gas and waste solids then pass through two post-reactor treatment zones (PRTZs). The first PRTZ is an insulated vessel which provides approximately 5 seconds of additional gas-phase residence time at approximately 1370°C . The second PRTZ is water-cooled. It primarily cools the gas to less than 540°C . Solids exiting the second PRTZ are collected in a bin which is sealed to the atmosphere as a safety precaution. Any solids remaining in the product gas are removed by a cyclone followed by a baghouse for fine particle filtration. The product gas then enters an aqueous caustic scrubber for chlorine removal. Any residual organics and chlorine are removed by activated carbon beds just upstream of the process stack. The product gas, essentially nitrogen at about 50% relative humidity, is then emitted to the atmosphere.

PCB (Aroclor 1260) was mixed with sand to form a solid feed containing approximately $3000\text{ }\mu\text{g/g}$ PCB. Carbon black was added to the feedstock at approximately a 6.25:1 ratio to the PCB oil to simulate the organic carbon content of soil. Carbon tetrachloride was mixed with screened, dried soil (less than 35 mesh) with CCl_4 concen-

tration approximately 0.37-13.76%. Activated carbon was added to the feedstock at 94:1 ratio (w/w) to CCl_4 to reduce the volatility of CCl_4 and to prevent its loss before reaching the reactor.

PCB test results reportedly show that, in all test cases, DREs exceeded 99.99999%, at least an order of magnitude greater than the requirement of the Toxic Substance Control Act (TSCA) regulations. Maximum PCB concentrations in the treated feed and baghouse filter catch were 0.001 $\mu\text{g/g}$ and 0.53 $\mu\text{g/g}$, respectively. These values are well below the TSCA limit of 50 $\mu\text{g/g}$ set for solids to be treated as hazardous wastes. Although results for the scrubber liquid were variable, ranging from 0.29 to 2.7 $\mu\text{g/l}$, all were well below the TSCA limit of 50 mg/l set for liquids to be treated as hazardous wastes. The results also reportedly show that PCDDs (dioxins) and PCDFs (furans) at the cyclone outlet were below analytical detection limits.

For the CCl_4 testing, its DRE results reportedly show values greater than 99.9999%. These results are at least two orders of magnitude better than RCRA requirements for hazardous waste incinerators.

Huber conducted triplicate tests in Borger, Texas on their 12" diameter reactors with OCDD (OCDD mixed with clean soils) in late October 1984. Feed concentrations up to 18000 ppb, by weight, and feed rates up to 15 pound/minute were used. In all cases, no OCDD or products of incomplete pyrolysis (PIPs) were reportedly detected.

Triplicate tests of TCDD

contaminated soils were conducted with the 3" diameter reactor at Times Beach, Missouri on November 13, 1984. Again, no dioxin or PIPs were reportedly detected.

Test Conclusion

The AER has reportedly been shown to be capable of producing extremely high operating temperatures and rapid heating rates resulting in high destruction efficiencies. Normal operating temperatures are in the range of 2200°C to 2760°C compared to approximately 1650°C for rotary kiln incinerators. Although there is little information in the literature for reactions at these temperatures, there is some empirical evidence that most organic compounds completely disassociate into their elemental states. Data from extensive testing also are reported to show that intermediate compounds from partial reactions of feed materials are not formed. Since these compounds can add to downstream clean-up requirements, their elimination would reduce costs for gas cleaning equipment.

The ability to use very low gas flow rates provides relatively long residence times and permits the use of smaller, less costly, off-the-shelf downstream gas cleaning equipment. The destruction capability of the AER combined with high-efficiency gas cleaning equipment appears to allow the achievement of DREs as close to 100% as a given application requires. The ability to use activated carbon beds also provides safety back-up for removing hazardous organics from the process gas if an equipment malfunction should occur.

Because it is electrically heated, the AER can operate over a wide range of conditions including:

chemical (oxidizing, reduced, or neutral), temperature (anything up to 2760°C), and pressure (partial vacuum to low positive). Under reducing conditions, oxygen-containing byproducts such as PCDDs and PCDFs should not be readily formed. Tests reportedly have verified this important characteristic. There are no significant concentrations of products such as organics, CO₂ and NO_x. This is an advantage in Air Quality Control Regions where these pollutants are a problem. The ability to operate under partial vacuum prevents leakage and greatly increases the safety of the process.

The AER has apparently achieved commercial status by receiving

certification to destroy PCBs on soils under TSCA. More extensive permits under RCRA are currently pending. The AER has also reportedly been recommended for evaluation to detoxify 500,000 tons of dioxin-contaminated soil in Missouri by the Office of Technology Assessment.

For the reasons outlined herein, Huber believes that the AER technology has inherent performance, safety and mobility advantages over comparably-sized rotary kiln incinerators for soils detoxification.

CONCLUSIONS AND RECOMMENDATIONS

1. Table 1 summarizes the research activities reviewed by this paper.

TABLE 1. SUMMARY OF PILOT-SCALE TESTING FACILITIES

Facility(Sponsor)	Type of Incinerator	Process	Capacity (MMBtu/hr)
1. CRF (EPA)	Rotary kiln with afterburner	Oxidation	3.6 (1.8 rotary kiln, 1.8 afterburner)
2. Acurex Facility (EPA)	Boiler	Oxidation	1.5
3. Mobile Incinerator (EPA)	Rotary kiln with secondary combustion chamber	Oxidation	15
4. CTT (EPA)	Liquid injection	Oxidation	0.15
5. Rotary kiln Incinerator Simulation (EPA)	Rotary kiln with afterburner	Oxidation	0.51 (0.35 rotary kiln, 0.16 afterburner)
6. Union Carbide Facility (Union Carbide)	Liquid injection	Oxidation	3.0
7. Mobile Plasma Arc Unit (EPA/ New York State)	Plasma arc reactor	Pyrolysis by conducted gas	1.7
8. Advanced Electric Reactor (Huber)	Electric reactor	Pyrolysis by radiation	3.4

2. Table 2 shows what compounds have been tested or are to be tested by which research institute.

3. Each of the compounds tested were generally destroyed to 99.99% or greater than 99.99% DRE.

4. The products of incomplete combustion are probably the most difficult to research in the overall area of hazardous waste thermal destruction. Almost every test produces some sort of PICs at ppm-ppb concentration levels. The question is "should ppm, ppb, or ppt concentrations of PICs concern

the public, the EPA or the technical community or not?" So far there is no answer.

5. Because PICs could be more hazardous than the original compounds, studying PIC formation and control should be one of the most important research areas that EPA and others could focus on.

6. Although there is a significant amount of experimental data, no analytical methods have been developed to predict what DREs or PICs would result if incinerator conditions change. Research is needed to fill that void.

TABLE 2. COMPOUNDS TESTED OR TO BE TESTED

Compound		Tested By	To Be Tested By
Acetonitrile			
(Methyl Cyanide)	CH ₃ CN		4
Benzene	C ₆ H ₆		
Chlorobenzene	C ₆ H ₅ Cl	2	4,7
1,2-Dichlorobenzene	C ₆ H ₄ Cl ₂	3	
1,2,4-Trichlorobenzene (TCB)	C ₆ H ₃ Cl ₃	1,3	4
1,2,3,4-Tetrachlorobenzene	C ₆ H ₂ Cl ₄	3	
Hexachlorobenzene (HCB)	C ₆ Cl ₆	1,8	
Biphenyl	C ₁₂ H ₁₀		
(Polychlorinated Biphenyls)			
Aroclor 1242	C ₁₂ H _{6.9} Cl _{13.1}		7
Aroclor 1254	C ₁₂ H ₄ Cl ₁₅		7
Aroclor 1260	C ₁₂ H _{3.7} Cl _{16.3}	3,8	7
Dioxin			
2,3,7,8 Tetrachlorodibenzo-p-dioxin	C ₁₂ O ₂ H ₄ Cl ₄	8	
Octachlorodibenzo-p-dioxin (OCDD)	C ₁₂ O ₂ Cl ₈	8	
Ethane	C ₂ H ₆		
1,2-Dichloroethane	C ₂ H ₄ Cl ₂	2	4
Hexachloroethane	C ₂ Cl ₆		4
Ethanol	C ₂ H ₅ OH		7
Ethylene	C ₂ H ₄		
Tetrachloroethylene	C ₂ Cl ₄		7
Hexachlorocyclopentadiene	C ₅ Cl ₅		7
Hexane	C ₆ H ₁₄		
Hexachlorohexane	C ₆ H ₈ Cl ₆		7
Methane	CH ₄		
Methyl Chloride	CH ₃ Cl	2	
Chloroform	CHCl ₃	2	4,7
Carbon Tetrachloride	CCl ₄	2,3,8	4,7
Methyl Ethyl Ketone	CH ₃ COC ₂ H ₅		7
Phenol	C ₆ H ₆ O		
2,4,6-Trichlorophenol	C ₆ H ₃ Cl ₃ O		7

Where 1 = EPA's Combustion Research Facility (CRF) at Pine Bluff, Arkansas

2 = EPA's Destruction of Hazardous Wastes Cofired in Industrial Boilers

3 = EPA's Mobile Incinerator at Edison, New Jersey

4 = EPA's Controlled Temperature Tower at Cincinnati, Ohio

5 = EPA's Rotary Kiln Incinerator Simulation at Research Triangle Park, N.C.

6 = EPA's/New York State's Fundamental Flame Combustion Research Program at Union Carbide

7 = Destruction of Hazardous Waste Using Plasma Arc Technology

8 = Destruction of Hazardous Waste Using Huber's Advanced Electric Reactor

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

EXPERIENCES WITH SPECIAL WASTE RECEPTION, INTERMEDIATE STORAGE
AND INCINERATION AT THE HAZARDOUS WASTE INCINERATION
PLANT AT BIEBESHEIM

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ABSTRACT

The Hazardous Waste Incineration Plant at Biebesheim has been in operation since early 1982. Technically, the plant is designed to accept, store and incinerate hazardous wastes, either solid, semi-solid, liquid or delivered in drums, for final disposal. Capacity: 60'000 t/a.

Due to the very strict official regulations on the max. permissible emissions, it became imperative to put very strong restrictions, with regard to flexibility and efficiency of the cleaning of the flue gases, on the flue gas purification plant. Important for the technical lay-out of the flue gas scrubbing plant was especially the stipulated separation of aerosols as well as the regulation that the total amount of arsenic, lead, chromium, cobalt and nickel must not exceed 1 mg/m^3 and that cadmium emissions must not exceed 0.16 mg/m^3 in the flue gas stream. Noxious substances, such as HCl , HF and SO_2 , must likewise be separated. Technical, local and environmental considerations as well as the well-known difficulties in separating various heavy metals (i.e. cadmium and mercury) from waste water of a flue gas treatment plant, led to the decision to apply the effluent-free flue gas scrubbing process.

The effluent-free flue gas scrubbing process has been in operation now for over 3 years. Meanwhile, three basic measurements have been carried out in the plant. The results of the measurements meet the demands of the authority. Both the test results and the operation results prove that the Hazardous Waste Incineration Plant at Biebesheim - especially the integrated effluent-free flue gas scrubbing process - meets the required standards of technology.

The Hazardous Waste Incineration Plant, Biebesheim was planned and built following a project lanced by the State of Hessen for the disposal of hazardous waste. Technically, it is designed to accept solid, semi-solid, liquid or also in barrels and drums delivered hazardous waste, including intermediate storage and thermal treatment.

In order to achieve optimum availability of the entire plant, two independently-operating incineration trains were installed. (Figure 1).

Plant Details

Each incineration train consists of the following plant units:

- waste reception and feeding installation
- rotary kiln with front wall assembly
- after-burning chamber
- boiler
- flue gas purification plant
- stack

HIM-VERBRENNUNGSANLAGE BIEBESHEIM

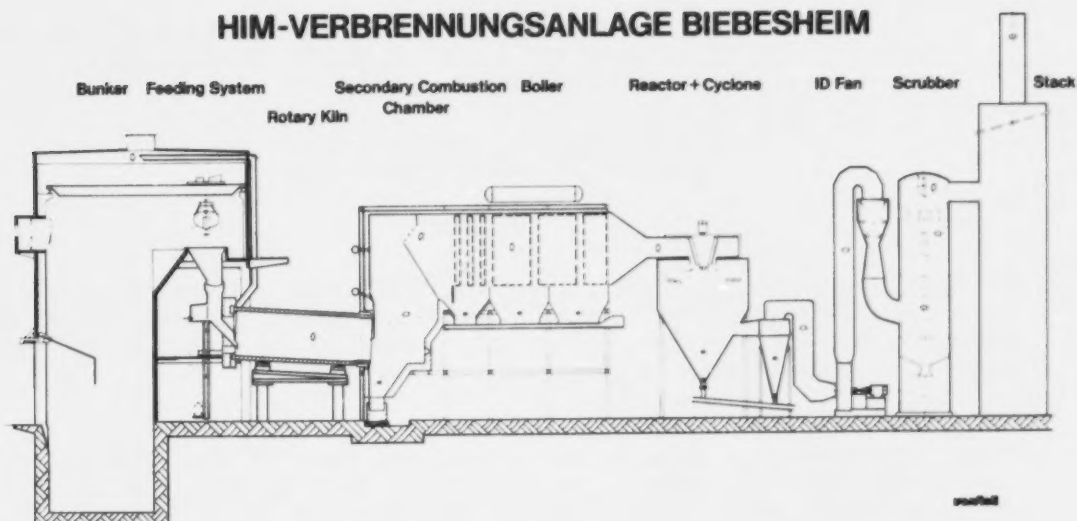


Figure 1.

Rated capacity of each incineration train (Figure 2):

- for liquid hazardous waste:
5.000 to 11.500 t/a
(16.730 to 29.300 kJ/kg)

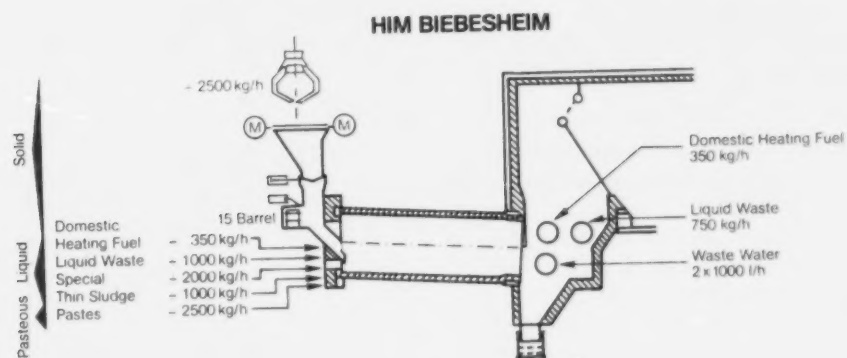


Figure 2.

- for solid and semi-solid hazardous waste:
13.500 to 20.000 t/a
(10.470 to 18.830 kJ/kg)

- additional organically contaminated water without significant heat value:
16'000 t/a

- heat release in the rotary kiln:
13.97 MW max. continuous rating
17.44 MW short time peak load
- heat release in the rotary kiln
and in the after-burning chamber
combined:
17.4 MW max. continuous rating
22.7 MW short time peak load
- total rated capacity of the
plant:
60.000 t/a

Waste Reception and Feeding Installation

The waste reception and feeding installation consist of:

- crane installation
- feeding hopper
- drum elevator
- semi-solids container and special pump for viscous liquids.

The reception and feeding installation is designed to enable the following material to be fed into the rotary kiln for thermal treatment through the front wall assembly:

- solid waste from the bunker
- liquid waste from the tank farm
- semi-solid waste delivered in barrels or drums

Rotary Kiln with Front Wall Assembly, After-burning Chamber and Steam Boiler

The entire combustion system consisting of rotary kiln with front wall assembly, after-burning chamber and steam boiler, is designed to allow for fluctuations in the composition of the semi-solid, liquid and solid waste within a

wide range and to enable direct corrective action to be taken in the kiln. The flow conditions in the rotary kiln and the after-burning chamber are devised to ensure effective admission of secondary air into the after-burning chamber (Figure 3).

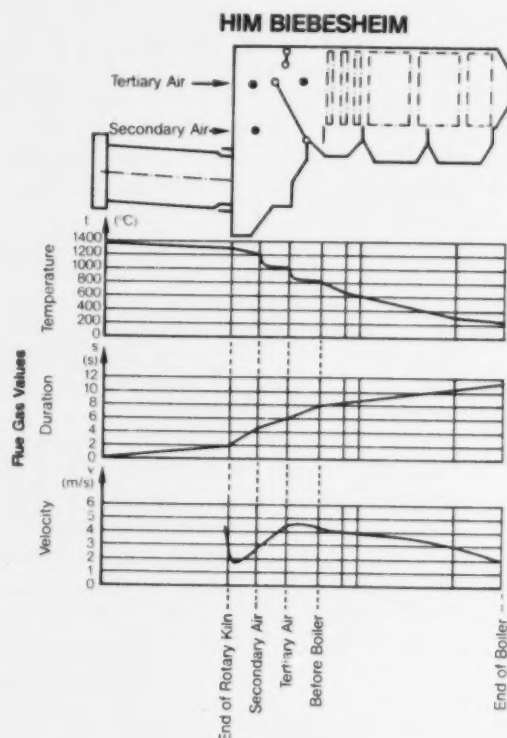


Figure 3.

The steam boiler system is a natural circulation, waste heat recovery design. The boiler is placed downstream of the uncooled after-burning chamber. In this way, a clear separation is established between the actual combustion process and gas cooling. New in the process in connection with the boiler, is the tertiary air introduction assembly

in the upper part of the after-burning chamber, which is an integral part of the boiler.

The tertiary air introduction effects a shock-like cooling of gases previously completely burnt-out in the after-burning chamber, from 1.200°C to 800°C. Thereby, the liquid and fused ash particles and salts carried in the gas stream are cooled down, so that it is possible to reduce the sticking properties of the fly ash which are known to develop during high temperatures. Consequently, sooting-up of the boiler surfaces is clearly reduced and the cleaning of the boiler surfaces by rapping is essentially facilitated. Cleaning is accomplished by vibration of the boiler tubes, generated by a rapping device located at the side of the boiler and operated automatically.

The low steam parameters (25.5 bar and 280°C) were deliberately selected to counteract fouling and consequent high temperature corrosions which occur in solid waste combustion plants operating with steam data of higher magnitude.

Flue Gas Purification

The incineration of organic hazardous waste and organically contaminated waters in the rotary kiln with after-burning chamber has long been technically proven. However, due to the stricter demands on the cleaning of flue gas, important new processes had to be introduced for separating hydrochloric acid (HCl), sulphur dioxide (SO₂), fluoride (HF), aerosols and heavy metals.

The following maximum permissible emissions were laid down in the official approval for the Hazardous

Waste Incineration Plant at Biebesheim:

- material of Class I
(max. 5 mg/m³)
- material of Class II
(max. 15 mg/m³)
- total dust
(max. 75 mg/m³)
- the total emissions of
Benz(a)pyrene
Dibenz(alpha,beta) anthracene
Beryllium and its compounds
- stated as Be - (max. 0.1 mg/m³)
- the total emissions of arsenic and its compounds - stated as As -
lead and its compounds - stated as Pb -
chromium - VI - compounds - stated as Cr -
cobalt and its compounds - stated as Co -
nickel and its compounds - stated as Ni -
(max. 1 mg/m³)
- the emissions of cadmium must not exceed 384 g/d (0,16 mg/m³)
- the gaseous emissions
chlorine compounds - stated as chloride (max. 100 mg/m³)
fluoride compounds - stated as fluoride - (max. 5 mg/m³)
- carbon monoxide (max. 100 mg/m³)
- emissions of carbon in combustible organic substances (max. 50 mg/m³)

The presence of aerosols, in particular also of heavy metal-oxides such as cadmium (Cd), lead (Pb), chromium (Cr), copper (Cu), vanadium (V) and zinc (Zn) in the flue gases of thermal treatment plants for hazardous waste, has been confirmed in various tests.

It was known that the absorption of acids, gaseous noxious substances and also dust particles of not-too-small grain size, can be effectively accomplished with relative ease in flue gas scrubbing processes.

Considerably more difficult to solve was the separation of aerosols from the flue gas. In order to achieve this, a "conditioning" of the aerosols was required, resulting in enlargement of the particles and so simplifying the separation procedure. This conditioning was attained by:

- agglomeration of numerous aerosol particles to larger particles
- adherence of water to these single particles

The separation of aerosols makes it possible to remove fine dust and metal oxides with an efficiency rate of at least 99.5%.

In order to prevent the problems, when utilizing a flue gas scrubbing plant, directly shifting from the air to the water, an extensive and expensive-to-operate waste water treatment plant is required to eliminate the heavy metals from the waste water. It was known, from operation of sewage treatment plants, that especially the separation of heavy metals - mercury (Hg) and cadmium (Cd) - from the waste water, is extremely difficult. Therefore - and in view of the local possibilities of effluent discharge - an effluent-free flue gas scrubbing process was selected for the Hazardous Waste Incineration Plant at Biebesheim.

Description of the Process

A simplified flow sheet illustrates the process basics of the effluent-free gas purification system (Figure 4).

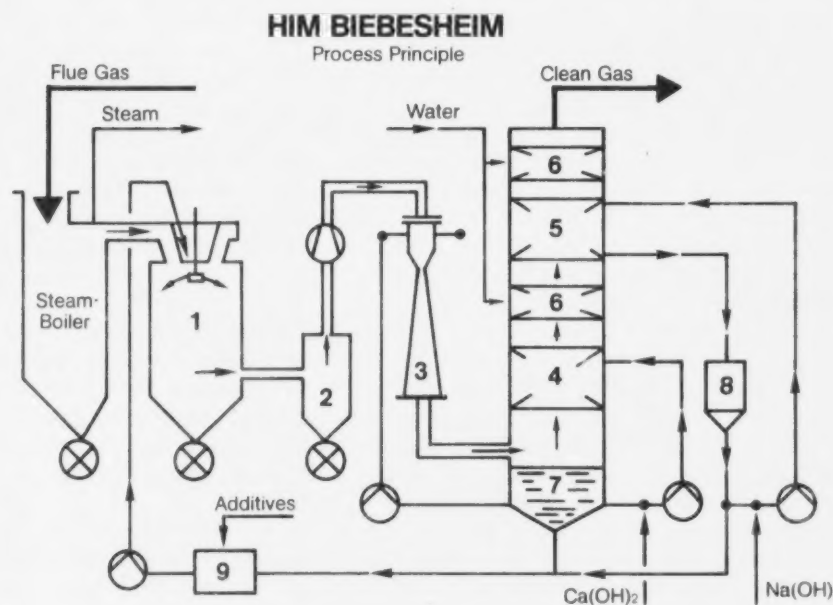


Figure 4.

In a first treatment stage, after leaving the boiler at a temperature of 250 - 280°C, the flue gases pass through the reactor (1) from the top downwards in parallel flow with the finely atomized liquid from the scrubber using a centrifugal atomizer. The required heat for evaporation of the scrubbing liquid is extracted from the flue gas.

Thereby, the flue gas is cooled from 250 - 280°C down to 160 - 180°C. In the reactor, a portion of the acid noxious substances, such as HCl, HF and SO₂ already adheres to the fine dust by settling, i.e. is neutralized.

At this stage, the dried solids, such as salts - together with fine dusts and heavy metals - are largely separated from the flue gas in the reactor and in the following cyclone (2). Following the drying process, the flue gases enter the scrubber by means of an induced draft fan.

The flue gases are cooled and at the same time already in the quench (3), a strong absorption sets in of the gaseous noxious substances HCl and HF. Meanwhile, a first conditioning takes place of the aerosols present in the flue gas and of the ones deposited by condensing during the cooling process. By separating acid gas components, the pH-value of the scrubbing liquid levels to 0 - 1.

The flue gases, cooled and pre-conditioned in the quench, pass to the second scrubbing stage (4), where the actual absorption of HCl, HF and the cooling down to the water dew point of approx. 70°C takes place. The pollutants HCl and HF are thereby separated, only leaving traces. The complete extraction takes place in the third scrubbing stage (5).

Besides the absorption process, especially that of HCl, HF and partly also of SO₂, the dust particles not caught by the cyclone, are extracted in the second stage.

The conditioned flue gases then pass on to the third scrubbing stage (5), via a droplet separating unit (6), which prevents the scrubbing liquor from being carried along.

In a venturi-intermediate stage located upstream of the third scrubbing stage, the suspended matter (aerosols) is pre-conditioned in such a way that it can be bound to the scrubbing liquor by means of 24 ring-jet elements which were especially developed for this purpose. Because of the extremely good absorption quality of the ring-jet stage (5) for gaseous material, this scrubbing stage also achieves an effective separation of SO₂. Caustic soda (NaOH) is added as neutralizer. After leaving the ring jet, the flue gas, together with the spray of the scrubbing liquor, passes to a short layer of filler material packing, which serves to agglomerate the fine liquid droplets so that they can be thoroughly separated by means of the directly following droplet separating unit.

Subsequently, the flue gases scrubbed free of gaseous noxious substances (HCl, HF and SO₂), fine dusts, aerosols (salt-condensates and heavy metal oxides) as well as liquor droplets, pass on to the stack.

Due to the satisfactory extraction of liquor droplets and aerosols, re-heating of the cleaned flue gases is not necessary.

Accompanying Measuring Programme

In line with the promotion of this project by the German Federal Ministry for Research and Technology (BMFT), an accompanying test and analysis programme is being carried out at the plant. A material and mass balance will indicate possible effects on the environment by the hazardous waste incineration plant which will be minimized by an appropriate optimizing process.

Official measurements to determine the degree of separation of the noxious substances have been carried out in the meantime, showing the following results.

	Approved Value in mg/m ³ (i. N. f.)	1. NUKEM Measure- ment in mg/m ³ (i. N. f.)	2. NUKEM Measure- ment in mg/m ³ (i. N. f.)	TA-Air Value in mg/m ³ (i. N. f.)
HCl	100	15	9	100
HF	5	0.03	0.5	5
SO ₂	200	100	115	—
CO	100	6	15	50
C (organic)	50	3	—	50
NO _x (calculated as NO ₂)	—	40	60	—
Dust, total	75	30	12	75
Dust, class I	5	3.5	1.3	20
Dust, class II	15	10	2.5	50
Cd	0.16	0.90	0.06	—

Table 1.

The following chart shows a comparison between the approved measured values and the TA-air values (German Clean Air Act - TAL 1974):

Metals	TUH Measure- ment in mg/m ³ (i. N.)	1. NUKEM Measure- ment in mg/m ³ (i. N.)	2. NUKEM Measure- ment in mg/m ³ (i. N.)
Arsenic (As)	0.03	0.03	<0.03
Beryllium (Be)	0.02	0.02	<0.02
Cadmium (Cd)	0.09	0.05	0.06
Cobalt (Co)	0.01	0.03	<0.03
Chromium (Cr)	0.05	0.06	0.12
Copper (Cu)	0.04	0.5	0.13
Mercury (Hg)	0.006	0.03	0.05
Nickel (Ni)	0.02	0.06	<0.06
Lead (Pb)	1.67	3.0	0.70
Zinc (Zn)	1.86	7.1	0.70

Table 2.

Operating Experiences

The Hazardous Waste Incineration Plant at Biebesheim has been operating since early 1982. As the flue gas scrubbing system of the plant has neither an emergency stack nor a bypass, the plant can only be operated when the flue gas cleaning system is available. There were no breakdowns in the flue gas cleaning system which could have considerably impaired the availability of the Hazardous Waste Incineration Plant at Biebesheim.

In 1982, the first year of operation - the year of start-up and the optimizing period of the plant - approx. 30.000 t of hazardous waste was processed: in the following years, 1983 and 1984, approx. 52.000 t resp. 60.000 t.

A larger deviation resulted only in the costs for repair and maintenance. This was due to the fact that the official authorities demanded an operating temperature in the rotary kiln of 1200°C which is effectively necessary for a satisfactory complete combustion. This, however, led to an attack by chemical and mechanical action on the kiln refractory. Therefore in place of the one-layer refractory, a 1.5 times thicker refractory layer is required per year.

Furthermore, the variety of waste material to be incinerated has greatly changed, compared with assumptions at the time the plant was designed. This especially refers to solid hazardous waste. In 1984 alone, the delivery of solid waste has increased by 100%.

Summing up, it can be stated that the concept of the Hazardous Waste Incineration Plant as well as the effluent-free flue gas cleaning system at Biebesheim is successful. All residues produced during combustion, such as slag, fly-ash and fine dust (salts and metals), accumulate in a dried condition.

The slag and fly-ash can be deposited on an industrial waste landfill. The salts, fine dusts and heavy metals, i.e. all residues from the reactor, must be packed in special containers because these are mainly water-soluble salts which must be taken to an underground deposit (Herfa-Neurode). In order to reduce the higher costs compared to storage on an industrial waste landfill, tests are carried out to determine whether, by special measures - i.e. by solidifying - it might be possible to deposit these residues on a normal industrial waste landfill.

Prospects

Due to the increased amount of hazardous waste, it is necessary to extend the plant by a third train. The experiences made during the present operation of the Hazardous Waste Incineration Plant at Biebesheim will result in important technical improvements which will be considered for the extension of the plant:

- Increasing the diameter of the rotary kiln, whereby, with regard to the actual waste situation, a higher throughput of solids will be achieved. At the same time, improved access to the burner and lances in the front wall assembly is achieved.
- Installation of an electrostatic precipitator instead of a cyclone for dust separation.

During operation, it became obvious that the solid particles formed in the reactor are so fine that a dust separation in the cyclone did not prove to be successful and the dust separation was transferred from the cyclone to the scrubber. This increased dust accumulation in the scrubber has, in no way, influenced the functioning of the scrubber: it has, however, led to an increased maintenance in the circulating pumps which could be decisively reduced by installing an electrostatic precipitator.

Disclaimer

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DEVELOPMENT OF PREDICTIVE MODELS FOR THE ASSESSMENT OF POLLUTANT EMISSIONS FROM INCINERATORS

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ABSTRACT

Considerable progress has been made over the recent years both on the experimental and theoretical aspects of flame combustion of hydrocarbons bearing hetero-atoms such as halogens (especially chlorine) nitrogen, and sulfur. In particular, the emerging results from carefully controlled studies of laboratory flames with the aid of molecular beam mass spectroscopy (MBMS) is leading to the establishment of better and more detailed insights of the chemistry of combustion taking place in incinerators. These developments, combined with the availability of fast computers, and reliable thermochemical kinetic data and accurate estimation methods is allowing us to develop comprehensive chemical kinetic models describing the detailed destruction mechanisms of the principal organic hazardous components (POHC) in waste streams. These detailed "engineering" models involve the participation of a large variety of intermediates in the combustion process, thus provide a rational starting point for the scientific assessment of the formation of products of incomplete combustion (PIC) from incinerators. Furthermore, these models, because of their comprehensive nature, allow the prediction of pollutant emissions from incinerators under conditions in which there are no prior experimental data available. This capability is particularly attractive in reducing costs related to expensive development and test runs.

INTRODUCTION AND PURPOSE

Combustion/ Incineration is an effective treatment process for the disposal of toxic and hazardous organic chemical wastes, which frequently contain compounds bearing hetero-atoms such as halogens, nitrogen, and sulfur. However, our understanding of the detailed chemistry of combustion of hydrocarbons containing such hetero-atoms is still at its early stages of development, inadequate yet to aid for the scientific design and operation of practical incinerators. As a result present day incineration technology is highly empirical in nature, and the technology is based primarily on information ac-

quired from large-scale test runs. Furthermore, it must also be recognized that whatever the information is available from such test-runs, it is of limited utility for predicting the performance of the incinerators under different set of operating conditions, i.e. the information has little predictive utility.

An important problem that is increasingly been recognized in the operation of practical systems is the inevitable formation of products of incomplete combustion (PICs) or the combustion intermediates, and their possible subse-

quent emissions from incinerators as pollutants. In fact, in many applications the potential emissions of these intermediates appear to be of greater concern than the principal organic hazardous constituents (POHCs) in the feed streams from public health point of view. For example, highly toxic COCl_2 (4,6) and HCN (12) form as intermediates during the incineration of chlorinated and nitrogenated hydrocarbons, respectively. It is therefore clear that the emissions of products of incomplete combustion will have to be considered as an integral part of the evaluation process for the scientific assessment of the performance of incinerators in the future, and thus for the successful utilization of this technology.

In recognition of this need our laboratories have pioneered a fundamental combustion/ incineration research program directed towards developing predictive chemical kinetic models that will be useful for the rational assessment pollutant emissions from incinerators. In our current research particular attention is given to study the incineration of chlorinated hydrocarbons (CHC) because of their large-scale presence in process waste streams, and because of their significantly different combustion characteristics when compared to other hetero-atom bearing hydrocarbons. For example, chlorinated hydrocarbons inhibit hydrocarbon oxidations in flames (18), exhibit two-step combustion reactions with the formation of highly toxic intermediates such as COCl_2 , even under oxygen rich conditions (4,5,6) and greatly promote the formation of polycyclic aromatic hydrocarbons and soot in flames (15).

In this communication, some of the recent experimental and theoretical developments on the incineration of model chlorinated hydrocarbons are presented, and the general principles involved in developing predictive models are described.

EXPERIMENTAL APPROACH

In order to develop rational chemical kinetic models with predictive capabilities the chemistry of incineration must be known with as much detail as possible. Otherwise, the process of constructing a comprehensive model becomes impractically cumbersome and complex. The most straight forward approach for this is to determine first the relative orders of formation and disappearance of many of the important intermediates during combustion, in which the presence of stable as well as radical species must also be considered. These requirements inevitably necessitate the use of molecular beam sampling methods (to preserve the integrity of flame radicals) coupled with line-of-sight mass spectroscopy.

Molecular beam mass spectroscopy (MBMS) is a highly versatile and powerful experimental technique which allows the direct determination of the chemical identity and relative concentrations of essentially all the species in flames, including the flame radicals in a single experiment. As a result, MBMS is most suitable in identifying the detailed chemistry and the relative rates of formation and destruction of products of incomplete combustion, during incineration.

Recently we have completed the construction of a state-of-the-art molecular beam mass spectrometer system for flame analysis, and began characterizing the incineration chemistry of chlorinated hydrocarbons (6). Other components in our research facility include precision flat flame burners (to generate one dimensional flames), a gas flow regulation system utilizing sonic orifices (to ensure pulseless and independent flows), a temperature control system (to uniformly preheat gases), and a microcomputer system for automatic data acquisition and for the control of experiments.

One dimensional flat flames are stabilized over a 5 cm. diameter flame holder which is also shrouded with an inert gas. The burner is mounted on a vertical translator which is motor driven and under computer control. The molecular beam sampling system as well as the mass spectrometer are mounted above the burner for line-of-sight detection of the species as shown in Figure 1.

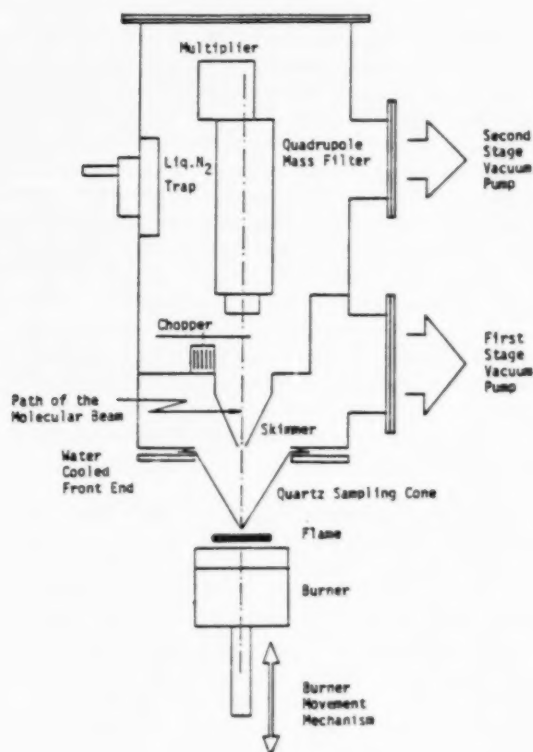


Figure 1. Schematic of the Molecular Beam Mass Spectrometer System

Flame sampling is accomplished by withdrawing gases from within the flame using a conical quartz cone with a cone angle of about 70-90 degrees and with an orifice at its tip having a diameter of about 30 microns. Upon passing through the orifice, the gases accelerate and form a supersonic jet and expand into the first vacuum stage of the MBMS system which is kept at about 10^{-4} - 10^{-5} torr by a 1000 lt/s turbomolecular pump. This level of vacuum is necessary to minimize

intermolecular collisions and thus to preserve the identity of flame radicals for mass spectroscopic detection. From the core of the expanding jet a molecular beam is obtained using the skimmer cone suitably placed above the quartz sampling cone. The molecular beam is ionized using electron impact ionization, pass through the quadrupole mass filter, and the appropriate signal intensities are detected. The molecular beam is also modulated at a fixed frequency in the range 150-400 Hz for the improved detection of species at low concentrations.

Data acquisition is accomplished by means of an analog/digital conversion board. The computer is programmed to read the beam signal intensity of the molecular ion that is being monitored directly from the lock-in amplifier and to move the burner relative to the quartz sampling cone in a predetermined sequence to generate species profiles along the flame. These species profiles are then used to identify the relative order of formation and destruction of the intermediates in the mechanism, and this information is subsequently used to develop detailed models.

In Figure 2, the temperature and some representative species intensity profiles measured along an oxygen rich $C_2HCl_3-O_2-Ar$ flat flame are shown. These profiles clearly illustrate the power of the MBMS technique in providing qualitative as well as quantitative information on the chemistry and mechanism of incineration of hazardous materials. These intensity profiles subsequently are converted into mole fraction profiles by using calibration-gas mixtures. The temperature profile was measured using a SiO_2 coated thermocouple.

METHODS OF DATA ANALYSIS

The experimentally determined species concentrations and their profiles are then used to construct detailed chemical kinetic models describing the incineration of the

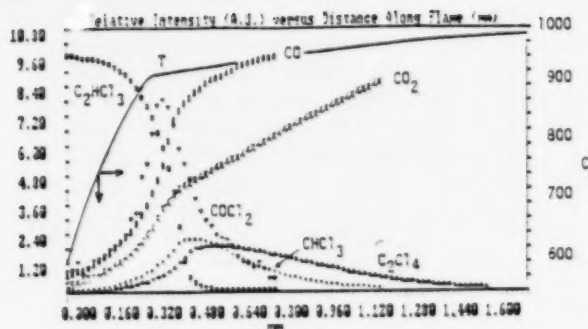


Figure 2. Temperature and MBS Species Intensity Profiles Along an Oxygen-Rich C_2HCl_3 Flat-Flame. (Note: Ordinate is in arbitrary units).

model hazardous compounds in an iterative fashion. Clearly these mechanisms must continually be revised as new and more accurate data becomes available, and when more definitive insights into the incineration processes develop.

In Table I a preliminary compilation of an elementary reaction set describing the incineration of C_2HCl_3 under oxygen rich conditions is shown. The mechanism involves the participation of about 40 species in about 100 reversible elementary reactions. This mechanism was constructed by systematically considering all the possible elementary reactions (steps) that may possibly be involved in the oxidation C_2HCl_3 and subsequently deleting and/or combining the reactions in the mechanism that are not supported by the experimental data and by the sensitivity analysis. For example, if the original mechanism involves the formation of a major intermediate species that cannot be measured in experimental flames, the reactions involving that species may be deleted and/or combined with other reactions. Similarly, if the relative importance of an elementary reaction is low (as determined by the sensitivity analysis) that reaction may also be eliminated and/or combined with other reactions. However, in many

cases the reactions may have to be left intact in the mechanisms for stoichiometric reasons, and for the broader applicability of the model. These will be discussed in more detail later.

In developing such detailed models, direct experimental measurements of individual elementary reaction rates are used whenever such data are available in the literature. There are a number of important compilations and discussions of elementary rate data involved in the oxidation of chlorinated hydrocarbons (2, 11), as well as reactions involving nitrogen and sulfur (19). When such rate information is not available they can be estimated with reasonable accuracy using theoretical methods (3, 10, 7, 8). Indeed, it is this ability to estimate the rate coefficients that allows us undertake detailed modeling studies. In this regard, these models should be viewed as "engineering" models, until each elementary reaction in the mechanism is studied in detail.

Another important element in modeling studies is the data base on the thermochemical and thermophysical properties of all the chemical species involved in the detailed model. The thermochemical information, which includes heats of formation, temperature dependent specific heat data, and specific entropy is as important as the elementary reaction rate data for the calculation of reverse reaction rates and temperatures. Such thermochemical data for many species are documented in convenient sources such as the JANAF Tables (16), and NASA compilations (1). However, such data for many of the intermediate and radical species are not generally available, consequently for those species the necessary thermochemical information must again be estimated using theoretical methods (3).

Table I
Detailed Chemical Kinetic Mechanism of Combustion of Trichloroethylene
($k = A T^{\frac{n}{E}} \exp(-E/RT)$, in cal., s, cc, mole units)

	Reaction	A	n	E	Reaction	A	n	E
1	C2HCL3 + M → C2HCL2 + CL + M	1.00E17	0	45000	C2HCL3 + C2HCL3 → C2HCL4 + C2HCL2	1.00E12	0	3000
2	C2HCL3 + M → C2HCL2 + HCL + M	1.00E16	0	55000	C2HCL3 + C2HCL3 → C2HCL4 + C2HCL2	1.00E12	0	3000
3	C2HCL3 + M → C2HCL2 + CL2 + M	1.00E14	0	40000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
4	C2HCL3 + CL → C2HCL4	6.31E13	0	0	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
5	C2HCL3 + O2 → C2HCL4 + HO2	1.00E12	0	5000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
6	C2HCL3 + CL2 → C2HCL4 + CL	4.79E11	0	5130	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
7	C2HCL3 + M → C2HCL4 + CL + M	1.58E14	0	47400	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
8	C2HCL3 + M → C2HCL4 + C2HCL2 + M	3.98E17	0	74700	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
9	C2HCL3 + CL → C2HCL4 + HCL	2.00E12	0	5100	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
10	C2HCL3 + M → C2HCL4 + CL + M	2.51E15	0	15500	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
11	C2HCL3 + O2 → C2HCL4 + CLO2	1.00E12	0	5000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
12	C2HCL3 + CL → C2HCL4 + CL2	1.00E14	0	20000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
13	C2HCL3 + CL → C2HCL4 + HCL	1.00E13	0	3000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
14	C2HCL3 + OH → C2HCL4 + H2O	1.00E13	0	2000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
15	C2HCL3 + OH → C2HCL4 + HOCL	1.00E13	0	1000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
16	C2HCL3 + CLO → C2HCL4 + CLO2	1.00E13	0	1000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
17	C2HCL3 + CLO → C2HCL4 + HOCL	1.00E13	0	1000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
18	C2HCL3 + O → C2HCL4 + CCL2	1.00E13	0	2000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
19	C2HCL3 + O → C2HCL4 + HCL	1.00E13	0	5000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
20	C2HCL3 + HO2 → C2HCL4 + H2O2	1.00E13	0	15000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
21	C2HCL3 + M → C2HCL4 + CL + M	1.00E17	0	73000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
22	C2HCL4 + O → C2HCL2 + CCL2	1.00E13	0	5000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
23	C2HCL4 + OH → C2HCL2 + HOCL	1.00E13	0	2000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
24	C2HCL4 + OH → C2HCL2 + CCL2	1.00E13	0	2000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
25	C2HCL4 + CLO → C2HCL2 + CCL2	1.00E13	0	2000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
26	C2HCL4 + CL → C2HCL2 + CL2	1.00E13	0	2000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
27	C2HCL3 + M → C2HCL2 + CL + M	1.00E15	0	20000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
28	C2HCL3 + CLO → C2HCL2 + CCL2	1.00E14	0	20000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
29	C2HCL3 + OH → C2HCL2 + HCL	1.00E13	0	0	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
30	C2HCL3 + O → C2HCL2 + CCL2	1.00E13	0	0	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
31	C2HCL3 + O2 → C2HCL2 + CLO2	1.00E12	0	10000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
32	C2HCL3 + C2HCL3 → C2HCL4 + C2HCL2	1.00E12	0	4000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
33	C2HCL3 + O2 → C2HCL2 + CLO2	1.00E12	0	5000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
34	C2HCL3 + M → C2HCL4 + CL + M	1.00E17	0	40000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
35	C2HCL3 + CL2 → C2HCL4 + CCL2	1.00E13	0	5000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
36	C2HCL3 + O2 → C2HCL2 + CLO2	1.00E13	0	15000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
37	C2HCL3 + CL → C2HCL4 + CCL2	1.00E14	0	10000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
38	C2HCL3 + O → C2HCL2 + CCL2	1.00E13	0	10000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
39	C2HCL3 + OH → C2HCL2 + HCL	1.00E13	0	10000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
40	C2HCL3 + O → C2HCL2 + CCL2	1.00E13	0	10000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
41	C2HCL3 + CLO → C2HCL2 + CLO2	1.00E13	0	10000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
42	C2HCL3 + OH → C2HCL2 + HCL	1.00E13	0	10000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
43	C2HCL3 + CL → C2HCL4 + CCL2	1.00E13	0	10000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
44	C2HCL3 + O → C2HCL2 + CCL2	1.00E13	0	10000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
45	C2HCL3 + M → C2HCL4 + CL + M	1.00E17	0	73000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
46	C2HCL3 + O → C2HCL2 + CCL2	1.00E13	0	14000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
47	C2HCL3 + O → C2HCL2 + CCL2	1.00E13	0	4500	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
48	C2HCL3 + CL → C2HCL4 + CCL2	1.00E13	0	3000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
49	C2HCL3 + OH → C2HCL2 + HOCL	1.00E13	0	3000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
50	C2HCL3 + M → C2HCL4 + CL + M	1.00E17	0	75000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
51	C2HCL3 + O → C2HCL2 + CCL2	1.00E11	0	4000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
52	C2HCL3 + O → C2HCL2 + CCL2	1.00E13	0	5000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
53	C2HCL3 + OH → C2HCL2 + H2O	1.00E13	0	1000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
54	C2HCL3 + CLO → C2HCL2 + CLO2	1.00E13	0	10000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
55	C2HCL3 + CL → C2HCL4 + CCL2	1.00E14	0	21000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
56	C2HCL3 + O → C2HCL2 + CCL2	4.72E12	0	3340	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
57	C2HCL3 + O → C2HCL2 + CCL2	1.00E12	0	30000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
58	C2HCL3 + O → C2HCL2 + CCL2	1.00E14	0	0	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
59	C2HCL3 + OH → C2HCL2 + HCL	1.00E13	0	0	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
60	C2HCL3 + CLO → C2HCL2 + CLO2	1.00E14	0	0	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
61	C2HCL3 + C2HCL3 → C2HCL4 + C2HCL2	1.00E12	0	3000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
62	C2HCL3 + O2 → C2HCL2 + CLO2	1.00E12	0	20000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
63	C2HCL3 + O → C2HCL2 + CCL2	1.00E14	0	2000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
64	C2HCL3 + OH → C2HCL2 + HCL	1.00E13	0	0	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000
65	C2HCL3 + CLO → C2HCL2 + CLO2	1.00E14	0	2000	C2HCL3 + C2HCL3 → C2HCL4 + M	1.00E12	0	3000

Thermophysical properties, such as the species diffusivities, the mixture viscosity and conductivity are normally calculated using well established techniques (13,17). Such properties are important for accurate simulation of flames in which transport via diffusion is as important as convection.

In Figures 3 and 4 calculated species profiles along an oxygen rich C_2HCl_3 flat flame are presented together with those determined in experimental flames. As evident from these figures, the model predictions are in excellent qualitative as well as quantitative agreement with the experimental measurements. This agreement is particularly important in view of the very fundamental nature of the proposed mechanism shown in Table I.

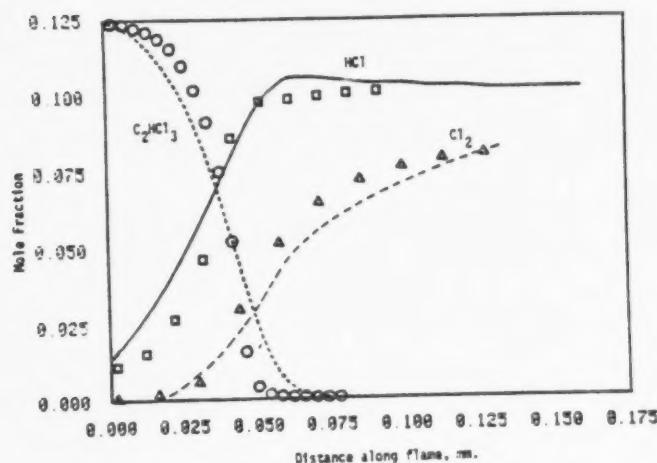


Figure 3. Calculated (lines) and Measured (symbols) Species Mole Fraction Profiles Along an Oxygen Rich C_2HCl_3 Flat Flame.

DISCUSSION

As evident from the mechanism presented in Table I, the oxidation of C_2HCl_3 involves the formation of a large number of stable as well as radical intermediates. The stable intermediates, which include species such as C_2Cl_4 , $COCl_2$, CCl_4 , and $CHCl_3$ constitute the obvious products of incomplete combustion

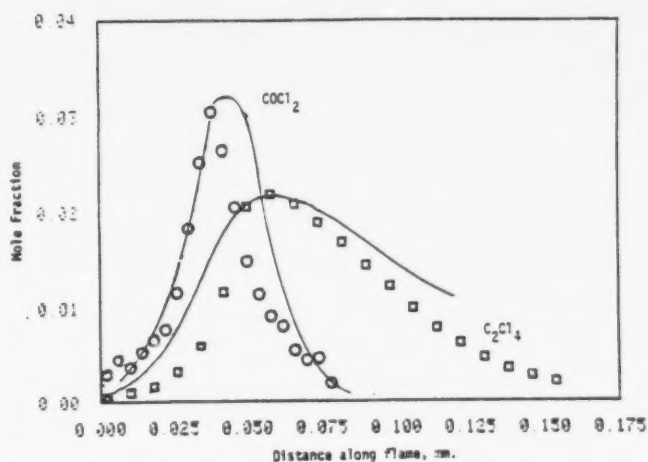
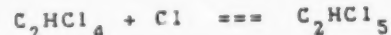


Figure 4. Calculated (lines) and Measured (symbols) Species Mole Fraction Profiles Along an Oxygen Rich C_2HCl_3 Flat Flame.

that may be emitted from incinerators burning trichloroethylene. Less obvious products of incomplete combustion are the recombination products of some of the flame radicals via reactions such as:



Therefore, Table I because of its comprehensive nature would be a rational starting point to assess the potential emissions of products of incomplete combustion from incinerators, and to predict the changing nature of these pollutants under different operating conditions. This will be accomplished by simply conducting numerical incineration experiments, rather than undertaking expensive test-runs.

Although the construction of smaller sets of reactions may be desirable from an engineering point of view, this may greatly reduce the range of applicability of the model (i.e. temperature, pressure, and composition range). For example, an elementary reaction which may be unimportant under oxygen rich conditions may become extreme-

ly important under oxygen lean conditions. Thus deleting that reaction from the mechanism based on oxygen rich experiments would greatly diminish the overall utility and the predictive capability of the mechanism.

Consequently, predictive models inevitably should involve a large set of reactions for safety. Furthermore, it must be noted that since calculation times are not dramatically influenced by the number of reactions, instead they are greatly influenced by the number of species in the mechanism, large sets of reactions are indeed acceptable in these studies.

One of the reasons why such detailed mechanisms are successful in simulating combustion/incineration processes is largely due to the fact that only a few of the reactions in the detailed mechanism are important in influencing the overall behavior of the incineration process under a given set of conditions. Therefore, the need for highly accurate rate information exists only for those dominant reactions in the mechanism. For the remaining reactions, the use of approximate rate data is usually sufficient. This is an important observation because experimentally measured rate data are not available for many of the elementary reactions shown in Table I, consequently they had to be estimated using theoretical methods. However, in spite of this the model predictions are in reasonable agreement with the experimentally determined species profiles.

The important reactions in the mechanism can also be identified by undertaking numerical sensitivity studies. Following their identification, these sensitive reactions may be isolated and studied individually for the accurate determination of their rate coefficients.

ACKNOWLEDGEMENTS

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

REACTION MECHANISM OF OXIDATION OF CHLORINATED METHANES

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ABSTRACT

Safe destruction of hazardous materials has become one of the major concerns of our society. Of particular importance are chlorinated hydrocarbons, which are major constituents of many industrial wastes. An effective way for the destruction of chlorinated hydrocarbons is incineration, which uses a flame environment to destroy these materials. In order to suggest appropriate operating conditions in existing incinerators and to ensure the effective destruction of hazardous wastes, one needs to develop an understanding of the physical and chemical phenomena which govern the process. The combustion chemistry of chlorinated hydrocarbons, the principal factor of the incineration process, is not well established. The goal of our current research program is to develop an understanding of this chemistry. This paper presents results of our modeling efforts directed towards the elucidation of the chemical reaction mechanisms for the oxidation of chlorinated hydrocarbons.

The initial efforts of our program are focused on detailed chemical kinetic modeling of the oxidation of chlorinated methanes, simulating the oxidation processes occurring at the experimental conditions of Miller et al. (1983). In that work, stoichiometric mixtures of chlorinated methanes/oxygen in argon were studied behind reflected shock waves at 1.8 atm. over the temperature range 1300-1600K. Monitoring pressure, the ignition delay times were determined. The objective of our modeling is to develop a reaction mechanism which would predict the experimental observations. The development of the reaction mechanism follows the procedures established previously (Miller and Frenklach, 1982, and Frenklach, 1984).

The modeling results for methyl chloride and dichloromethane were reported recently (Miller et al., 1985). This paper presents the results for chloroform and carbon tetrachloride. Discussion of reaction mechanisms composed of elementary chemical reactions and the computational prediction, using the developed mechanisms, of the corresponding experimental observations are presented. Comparing the mechanisms for methane, methyl chloride, dichloromethane, chloroform and carbon tetrachloride the influence of increased chlorination of methane on the reaction mechanism is discussed.

TIER 4 DIOXIN TEST PROGRAM STATUS

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ABSTRACT

The paper discusses the status of Tier 4 of the National Dioxin Study and focuses primarily on the identification and selection of candidate combustion sources for the test program. No laboratory results will be presented.

The Tier 4 program addresses the broad questions do combustion sources emit significant quantities of dioxin? If so, how much and what are the health risks associated with these emissions?

The approach taken to address these questions was divided into several steps. First, an extensive literature search was conducted, and all available dioxin emissions data were summarized. The information was then analyzed to attempt to identify factors which would affect dioxin emissions from combustion sources. The analysis indicated that the following factors could have an effect on dioxin emissions.

- Presence of dioxins in the feed;
- Presence of dioxin precursors in the feed;
- Chlorine in the feed;
- Combustion conditions (temperature, oxygen level, etc.); and
- Feed processing.

The analysis also indicated that combustion of waste products as opposed to fossil fuels was more likely to form dioxins. Using the factors listed above, in conjunction with a list of major combustion source categories and the available dioxin emissions data base, a ranked list of combustion source categories with the potential to emit dioxin was developed.

In conjunction with the development of the list, a source test program was devised. Ten to twelve sources are to be tested for dioxin emissions using a Modified Method 5 sampling train including an XAD-2 resin trap. The test program also includes sampling of feed materials and collected particulate; continuous monitoring of CO, CO₂, O₂, and THC; and acquisition of operating data over the period of each test. In addition, some 40 sites were selected for ash sampling and analysis to broaden the dioxin data base.

Site selection for the test program began in August 1984, and the first test was conducted in October. Two tests were conducted in November, and subsequent tests were conducted in December and January. All testing will be complete by June of 1985. No results from the test program are available.

INTRODUCTION AND PURPOSE

The Air Management Technology Branch (AMTB) within the EPA's Office of Air Quality Planning and Standards (OAQPS) is responsible for the development and implementation of a source testing program for Tier 4 of the National Dioxin Study. Technical guidance for the source test program is provided by IERL/HWERL in Cincinnati. The purpose of Tier 4 is to assess combustion source emissions of polychlorinated dibenzo-p-dioxin (PCDD), with a focus on the most toxic isomer -

2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). Combustion source emissions of polychlorinated dibenzofuran (PCDF) will also be addressed in this study.

Radian Corporation, under task order contract, is providing support to the AMTB by collecting and reviewing available literature data on emissions of PCDD's and PCDF's from combustion sources. In addition, Radian will perform PCDD

emissions tests on twelve combustion sources. The samples will be analyzed by EPA laboratories for PCDD's and PCDF's. The source test plan addresses the following questions:

1. Which combustion source categories emit PCDD's (and PCDF's) to the atmosphere?

2. What range of concentrations and quantities of PCDD's (and PCDF's) are emitted from these source categories?

3. What are the estimated health risks associated with these emissions?

This paper describes development of the source test program including selection of candidate combustion sources. In addition, the status of the program as of April 1985 is discussed. Further details of the program can be found in the project plan (1), the initial literature review document (2), and the sampling guidance manuals (3, 4) developed for the program.

Dioxins are members of a family of organic compounds known chemically as dibenzo-p-dioxins. All dioxin compounds have a three ring nucleus containing two benzene rings interconnected by a pair of oxygen atoms. The structural formula of the dioxin nucleus and the convention used in numbering its substituent positions are shown in Figure 1a. Chlorinated dioxins can contain up to eight chlorine atoms and 75 different chlorinated dioxins are possible. Each congener has its own physical, chemical, and health effects properties.

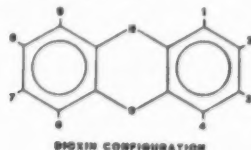


Figure 1a.

Dibenzofurans are a group of organic compounds that have a similar structure to the dibenzo-p-dioxins, except that the two benzene rings in the nucleus are interconnected with a five member ring containing only one oxygen atom (Figure 1b). Theoretically, the chlorinated dibenzo furan group can contain up to 135 different structural congeners, each

with varying physical, chemical, and health effects properties.

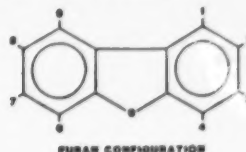


Figure 1b.

Of all the PCDD's and PCDF's 2,3,7,8-TCDD has received the most attention. However, in general, 2,3,7,8-TCDD represents a small fraction of the total PCDD found in combustion source emissions. In addition, PCDF emissions can exceed 2,3,7,8-TCDD emissions by two to three orders of magnitude. For some sources PCDF's contribute significantly (over 80 percent) to the health risk associated with combined PCDD and PCDF emissions.

APPROACH AND SCOPE OF THE TIER 4 STUDY

The Tier 4 program was divided into three phases: (1) the literature evaluation and design of a test program and (2) the source test program including ash sampling, and (3) data summary and analysis.

The first phase of the Tier 4 study was accomplished in three general tasks. The first task was to obtain and review the available literature on PCDD emissions from combustion sources. Over 100 published and unpublished reports were obtained. In addition, contacts were made with key individuals to identify recently performed or ongoing studies that could be used to supplement the data base. The second task was to develop a ranked list of source categories with potential to emit PCDD's. The criteria used to develop the ranked list was based on information obtained from the literature review. The final task was to develop a testing program to assess PCDD (and PCDF) emissions from combustion sources. The results of these tasks are summarized below.

PCDD Emissions Data

A review of the literature has produced a list of 12 broadly defined source categories for which some dioxin

emissions data has been collected. Table 1 lists sources for which published dioxin data could be found and summarizes the measured TCDD concentrations. Although the National Dioxin Study is focusing on 2,3,7,8-TCDD, most of the data found in the literature addressed TCDD and total PCDD. Since 2,3,7,8-TCDD data are limited, TCDD was used during the evaluation of the data base as the best indicator of 2,3,7,8-TCDD emissions.

with over 100 ppm chlorine and normally some chlorinated phenol content. The highest TCDD emissions are generally associated with solid feed fuels and low combustion temperatures. Combustion sources burning fossil fuels tended to emit less TCDD's than those burning waste products.

TABLE 1.
COMBUSTION SOURCES IDENTIFIED IN THE 1984 LITERATURE SURVEY (2)

Source Category	Number of Facilities Tested	Sample	TCDD ^a		2,3,7,8-TCDD	
			Mean	Range	Mean	Range
Municipal Waste Combustors						
USA	6	Stack	3.5 ng/m ³	ND-240 ng/m ³	3.5 ng/m ³	0.30-9.1 ng/m ³
European	13	Stack	25.6 ng/m ³	ND-178 ng/m ³	^b	-
Hazardous Waste Incinerators						
Incinerator Ship	2	Stack	ND ^c	ND	-	-
Land Based Incinerators	10(7) ^d	Stack	0.56 ng/m ³	ND-2.5 ng/m ³	ND	e
Sewage Sludge Incinerators	1	Stack	f	f	-	-
Utility Coal Boilers	7	Stack	ND	ND	-	-
Commercial Boilers (Waste Fired)	6(6) ^d	Stack	g	g	-	-
Industrial Boilers (Waste Fired)	6(1) ^d	Stack	10.13 ng/m ³	ND-40.5 ng/m ³	18,000 ppt ^h	ND-99,000 ppt
Activated Carbon Regeneration	1	Stack	0.013 ppt	ND-0.050 ppt	0.019 ppt	ND-0.043 ppt
Residential Wood Combustion	4	Scrapings	329 ppt	ND-777 ppt	242 ppt	26-600 ppt
Mobile Sources	9(4) ^d	Exhaust	4.0 ppt	ND-20 ppt	3.0 ppt	*
Wire Reclamation Incinerators	1	Scrapings	234 ppt	58-410 ppt	-	-
Lime/Cement Kilns (Waste Fired)	1(1) ^d	Stack	g	g	-	-
Accidental Electrical Equipment Fires	2	Wall Swipes	44 ppm ⁱ	ND-195 ppm	0.059 ppm	*

^aTCDD = Tetrachlorodibenzo-p-dioxin.

^bDash = No Data.

^cND = None detected (Detection limits vary).

^dNumber of tests have been performed, but the results have not been officially reported.

^e = One datum, no range available.

^fPCDD scan only. PCDD concentrations ranged from 483 ng/m³ to 1,140 ng/m³ with a mean of 739 ng/m³.

^gResults have not yet been officially reported.

^hppt = Parts per trillion by weight.

ⁱFuels include wood, wood/oil mixture, and natural gas.

^jFuels include diesel, unleaded and leaded gasoline. In one test series, exhaust scrapings were analyzed, in the other series, filter medium from exhaust samples.

^kIncludes PCB transformers and capacitor batteries.

^lppm = parts per million by weight.

A general characterization of each of the 12 source categories identified in the initial literature survey was made to identify similarities and differences that may affect the magnitude of PCDD emissions from each source. The following broad characteristics emerged. The source categories with the highest TCDD emissions were burning waste materials

Experimental Studies

In addition to gathering PCDD emissions data, all available experimental studies concerning PCDD formation mechanisms for combustion sources were obtained and reviewed in order to identify more specific factors that may contribute to PCDD formation.

There are several unproven hypotheses concerning PCDD emissions from combustion processes. Dow Chemical's "Chemistries of Fire" theory proposes that PCDD's are a natural byproduct of fire and will be formed at some quantities in all combustion processes (5). However, experimental results by Buser and Rappe (6) and an evaluation of data from the literature suggests that PCDD's are emitted only under limited conditions. The most prevalent theories, including Esposito's formation mechanism (7), involve the incomplete combustion of PCDD's or PCDD precursors. Although there is some disagreement of the definition of PCDD precursors, they are defined in this paper as chlorinated aromatics that can product PCDD's through bimolecular reactions and thermal rearrangements. Examples include chlorinated phenols and chlorinated benzenes. PCDD precursors may be thermally rearranged during incomplete combustion to form PCDD's. Also, when PCDD's are present in the feed to a combustion source, they can escape with the fine particulate if the destruction efficiency is low.

Neither the Dow hypothesis nor the precursor hypothesis is conclusively supported or refuted by the available data. Recent studies involving pyrolysis of wood with and without chlorination, in conjunction with studies of pyrolysis of chlorinated coal, suggest that any organic material combusted in the presence of high levels of inorganic chlorine may lead to PCDD formation under certain conditions.

Based on the literature review, the following factors are believed to affect dioxin emissions:

- Waste composition
 - PCDD In feed,
 - Precursors in feed,
 - Chlorine in feed,
- Combustion conditions
 - Residence time,
 - Oxygen availability,
- Waste characteristics
 - Feed processing, and
 - Supplemental fuel (variability and Btu value)

The interaction of these factors in PCDD formation mechanisms is not well understood. In addition, quantitative data concerning waste compositions is generally not available for many waste materials that are combusted and combustion conditions are not well defined for many combustion devices and are largely determined by site specific operating practices.

Source Category Prioritization

Despite these limitations the factors listed above in conjunction with available TCDD emissions data were used to subjectively rank all combustion sources for the purpose of the Tier 4 source tested program. A short list of combustion sources was developed by excluding those sources burning or using a relatively clean feedstock or fired with fossil fuels, such as coal, oil or gas, and those source categories which are fairly small or intermittent in nature, examples include incinerator ships and coffee roasting. The remaining sources were then divided into 4 groups ranked A-D using the rationale outlined in Figure 2. The ranks are defined as follows:

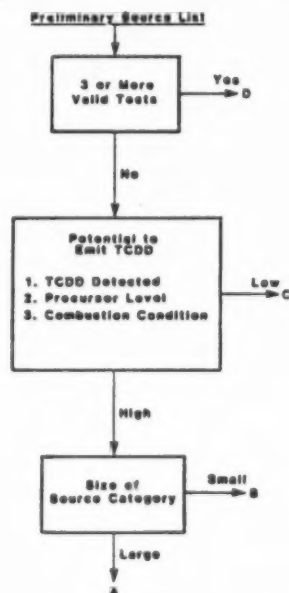


Figure 2. Ranking Flow Chart.

Rank A are large source categories (greater than 1 million tons of fuel and/or waste burned annually) with elevated dioxin precursor contamination of feed/fuel. These categories are judged to have a high potential to emit TCDD. Rank B are small source categories (less than 1 million tons of fuel and/or waste burned annually) or source categories with limited dioxin precursor contamination of feed/fuel. These categories have some potential to emit TCDD. Rank C are source categories less likely to emit TCDD. Rank D are source categories which have already been tested three or more times.

The ranked list was then used as the focus of the source test program. Preliminary cost estimates indicated that only 10-12 source tests could be performed with the available budget. With this limitation in mind, a decision was made to test three facilities for each of the two rank A source categories, and a single facility in each of the rank B categories. Through supplementary coordination with other in-house programs, samples were also planned for mobile sources and woodstoves.

Test site selection began in August 1984. This effort was initially focused on the rank A categories, sewage sludge incinerators and black liquor boilers. The site selection process involved identifying candidate sources from lists of sites provided by State and EPA Regional offices, trade associations and previous EPA studies. The lists were narrowed to three or four candidate sites using data on facility size, age, type of combustion device, etc. Each of the candidate sites on the short list was then contacted by telephone to explain the Tier 4 program, to gather further site specific information, and to ascertain if they were interested in participating in the program. Pretest survey visits were conducted at least two candidate sites per source category. For the rank A source categories, an attempt was made to pick at least one average source within the source category and one worst case candidate. For the rank B categories, attempts were made to select worst case sites with respect to PCDD emissions.

As the program progressed it became evident that it was very difficult to define the conditions which constitute worst case with respect to potential PCDD emissions. Very little if any PCDD or precursor information was available for the selected source categories, and the relative combustion conditions within the source category were not always known. For these reasons, a great deal of reliance was placed upon the total chlorine content of the primary feed materials to the combustion device as an indication of worst case conditions. For example, further information was found concerning the sources and levels of chlorides in black liquor circuits at Kraft pulp mills. During the initial source category selection process, black liquor boilers associated with the pulping of salt laden wood were suspected of having the highest chlorine content. After visits to numerous mills a brief literature survey and receipt of chlorine analyses for several mills it was discovered that very little wood is now stored in salt water prior to pulping. In addition black liquor with chlorine contents of 0.1 percent to 2 percent have been identified and a study was found which discussed the potential for chlorobenzene formation from combustion of black liquor (8). The highest chlorine content black liquor was associated with a mill that uses spent acid from the chlorine dioxide generator as a source of salt cake make up.

As the site selection process continued, additional source category specific data became available, and as a result, some changes were made to the ranked list. Table 2 presents the initial and final ranked list. The changes to the list are briefly discussed below. Commercial boilers firing waste oils were dropped from the rank A category because the proposed RCRA amendments would preclude the burning of waste oils blended with chlorinated solvents as other hazardous wastes. Combustion of wood treatment plant sludges containing pentachlorophenol and/or creosote (K001 waste) in boilers was identified as a rank B candidate in the initial list. Following contacts with the major wood treating companies and with various regulatory agencies, this category was dropped from rank B to rank C. All of the wood treatment companies claimed to be either landfilling the sludge or incinerating the sludge in a hazardous waste incinerator.

TABLE 2. RANKED SOURCE CATEGORY LISTS FOR PCDD TESTING

Initial List - March 1984	Current List - March 1985
Rank A Sewage Sludge Incinerators Black Liquor Boilers Commercial Boilers	Sewage Sludge Incinerators Black Liquor Boilers
Rank B PCP Sludge Carbon Regeneration Charcoal Manufacture Wire Reclamation	Carbon Regeneration Wire Reclamation Industrial Incinerators Salt-Laden Wood Fired Boiler Secondary Metals Blast Furnace Drum & Barrel Furnace
Rank C Mobile Sources Wood Stoves Wood Fired Boilers Small Spreader Stoker Hazardous Waste Incinerators Lime/Cement Boilers	Mobile Sources Wood Stoves Small Spreader Stoker Commercial Boiler PCP Sludge Lime/Cement Boilers
Rank D Municipal Waste Industrial Boilers Firing Hazardous Waste Hazardous Waste	Municipal Waste Industrial Boilers Firing Hazardous Waste

Charcoal manufacturing facilities were dropped from rank B to rank C because all facilities contacted were processing untreated forest scraps and not sawmill slabs that might have been pretreated with chlorophenols for Sapstain control.

In addition to these changes in the source category ranking, three categories were added to the source test program; these are industrial incinerators, secondary metals blast furnaces, and drum and barrel reclamation furnace.

Several industrial incinerators were identified during the course of the site selection process. Further investigation showed this to be a large category in terms of numbers of units nationwide (9). Solid waste materials burned in these units often contain appreciable levels of chlorine. In addition, most incinerators are fairly small and batch fed resulting in poor combustion conditions. One site selected for Tier 4 testing burns polyvinyl chloride (PVC) coated wood scraps

that have been treated with pentachlorophenol. The secondary metals blast furnace source category was also added to the source test list. Some blast furnaces in the secondary metals industry process metal bearing scrap that contains plastics including PVC (10). PCDD has previously been detected in the baghouse dust from one such facility.

Drum and barrel reclamation furnaces were added to the list because of the large number of facilities, the diverse nature of waste materials combusted during the drum burning process and because of the relatively poor combustion conditions encountered (11).

The Source Test Program

A total of twelve complete source tests will be conducted as part of the source test sampling program. The anticipated schedule is shown in Table 3. In addition, one woodstove will be sampled and two mobile source samples will be analyzed. The test program is

complex and involves characterization of combustion device conditions using continuous emissions monitors in addition to Modified Method 5 sampling for PCDD's following the draft ASME protocol (12). Samples of the feed materials to the combustion device will be sampled and analyzed for chlorine and precursor content. Ash and soil samples will be collected and analyzed for PCDD's. The sample matrices for the first 5 tests are shown in Table 4.

All testing is expected to be completed by July 1, 1985. Only limited PCDD analytical results are available at this time. All results will be presented in the final Tier 4 report which is scheduled for completion in late 1985. Results of the study will also be included in a report to Congress scheduled for December 1985.

Ash Sampling

A total of 40 ash samples will be collected for combustion sources selected by EPA regional offices. Analysis of these samples will supplement the source test data.

TABLE 3. TIER 4 SOURCE TEST SCHEDULE

Test Number	Schedule	Source Category
1	October 1984	Sewage Sludge Incinerator #1
2	November 1984	Industrial Incinerator (Wood/Plastic)
3	November 1984	Sewage Sludge Incinerator #2
4	December 1984	Black Liquor Boiler #1
5	February 1985	Black Liquor Boiler #2
6	March 1985	Wire Reclamation Incinerator
	March 1985	Wood Stove*
7	April 1985	Wood Fired Boiler
8	April 1985	Black Liquor Boiler #3
9	May 1985	Industrial Carbon Regeneration Furnace
10	May 1985	Secondary Metals Blast Furnace
11	June 1985	Sewage Sludge Incinerator #3
12	June 1985	Drum and Barrel Reclamation Furnace or Coal Fired Spreader/Stoker Boiler

*This test is being conducted jointly with an AA EPA program, the Integrated Air Cancer Project.

TABLE 4. SUMMARY OF TIER 4 SAMPLE MATRICES

Sample Stream	Site 01 SSI-A	Site 02 ISW-A	Site 03 SSI-B	Site 04 BLB-A	Site 05 BLB-B
Primary Feed Materials	Sewage Sludge	Wooden Wastes	Sewage Sludge	Black Liquor	Black Liquor
Auxiliary Fuels	No. 2	No. 2	None Fuel Oil	None Fuel Oil	None
Combustion Air	Yes	Yes	No	No	No
Combustion Device Outlet	CEM, MM5	CEM, MM5, HC1	CEM	CEM, MM5	CEM, MM5
Control Device Outlet	MM5	NA	MM5	MM5, HC1	MM5, HC1
Combustion Device Bottom Ash	Yes	Yes	Yes	NA	NA
Emission Control Device Ash	Scrubber Blowdown	NA	Filtered Scrubber Blowdown	No	No
Other Plant Materials	No	No	No	Yes	Yes
Soils	Yes	Yes	Yes	Yes	Yes

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

THERMAL CLEANING OF SOIL CONTAMINATED WITH CYANIDE WASTES FROM FORMER COAL GASIFICATION PLANTS

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ABSTRACT

The thermal cleaning of polluted soils from coal gasification plant sites was studied, both in laboratory experiments and in a 500 kg/hr pilot plant. The soils investigated were contaminated with a mixture of iron cyanide complexes (e.g. Prussian Blue $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) and polynuclear aromatic hydrocarbons (PAH's) in concentrations ranging from 1-2.5 g CN/kg and 30-180 mg PAH/kg, respectively.

To decompose the cyanide complexes, temperatures of 300-350 °C and a residence time of 30 min are necessary. Residual cyanide concentrations then vary from 3 to 17 mg/kg. Under these conditions, PAH's are removed as well, with residual concentrations below the detection limit of 0.01 mg/kg. The cyanide complexes decompose into a mixture of hydrogen cyanide (HCN) and cyanogen ((CN)₂), both gaseous compounds which can be incinerated.

These conditions were shown to be valid too for the pilot plant. At an oven wall temperature of 440 °C (soil temperature ca. 350 °C), soils contaminated with 40-130 ppm cyanide were cleaned to a residual level of 1-4 ppm.

A study on a laboratory scale of the incineration of HCN showed that temperatures of ca. 1100 °C are sufficient for > 99% combustion at contact times of 0.4-2 sec. A marked influence of the oxygen concentration on the incineration yield was observed. Increasing the O₂ concentration from 3.1 to 13.5 %, decreased the temperature necessary for incineration with about 100 °C.

The pilot plant incinerator was shown to be more than 99.9 % effective at 1050 °C with HCN concentrations in the off-gas of 0-2.5 µg/m³.

INTRODUCTION AND PURPOSE

In the past, town gas was prepared in The Netherlands by gasification of coal to produce a mixture of mainly methane, carbon monoxide and hydrogen (CH_4 , CO , H_2). This gas mixture was purified by removal of inorganic compounds like hydrogen cyanide (HCN) and sulfide (H_2S) and organic compounds like polynuclear aromatic hydrocarbons (PAH) and phenols.

For the removal of HCN so called "iron boxes" were used, in which the cyanide was bound as iron complexes like Prussian Blue $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. In fact a very complex mixture of iron cyanides and sulfides resulted, which was stored before further processing or (un)intentionally dumped on the terrain.

Now that town gas plants are no longer in operation, severe soil pollution problems remain. Concentrations of cyanide in the form of complex cyanides of up to 20 g/kg can be found in The Netherlands, mostly in combination with alarming amounts of PAH's, phenols and sulfur compounds.

Thermal cleaning of these soils seems promising as it may be expected that at high temperatures the organic compounds are volatilized and the cyanides decompose to form iron oxide and gaseous cyanide compounds. Incineration of the decomposition products may complete the cleaning process.

Several systems have been developed to heat the contaminated soil. In direct heating systems, the soil is heated by burners in a rotating tube oven or a fluidised bed oven. Large amounts of burning gasses are produced which must be processed together with the volatilisation and decomposition products.

We investigated and developed an indirect heating system in which a rotating tube oven is heated externally by a series of burners. The burning gasses are not mixed with the gaseous decomposition and volatilisation products of the soil, which gives an advantage in the design of the incinerator, where we now have to process the decomposition products from the soil only.

The gas flow in the tube oven is reduced, which causes less dust material to be transported to the cyclone and the incinerator.

Finally, the oven temperature is better controlled which is a distinct advantage in the case of the treatment of soils contaminated with organochlorine compounds.

APPROACH

Characterization of Cyanide Soils

Three types of cyanide soils, originating from different locations in the Netherlands were used in this investigation. The soils were characterized by quantitative analysis of the "free" and "total" cyanide, and the PAH's. For general characterization the pH and the total residue on drying at 105 °C were determined. The three soils will be designated as A, B and C.

Whenever concentrations are given in this paper, concentrations on dry weight basis are meant.

Total cyanide determination.

Samples of 5-10 g of polluted soil were suspended in 100 ml of distilled water. After addition of 15 ml of concentrated HCl , 10 ml of 0.8 M CuSO_4 solution, 2 ml of 1.8 M SnCl_2 solution in 0.5 M HCl , and 1 ml of a 1 % CdSO_4 solution, the suspension was refluxed for 90 min. The HCN formed, was collected in 50 ml of 1.25 M NaOH by passing a gentle stream of nitrogen through the suspension.

The final alkaline cyanide solution was used for the cyanide determination according to Standard Methods and EPA procedures (1,2).

Free cyanide determination.

Free cyanide was determined as described above, but with the omission of the CuSO_4 solution, which is the catalyst for the decomposition of the complex cyanides.

Determination of polynuclear aromatic hydrocarbons.

Basically the procedure according to Giger and Schaffner (3) was followed, with some modifications which were necessary due to the nature of the samples.

A sample of 6-10 g (wet weight) was extracted by sonication with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$. After addition of water the CH_2Cl_2 layer was isolated and concentrated to a volume of 5-10 ml.

Elemental sulfur was removed by elution over a copper column. The extract was further purified by chromatography on subsequently, Sephadex LH-20 with benzene-methanol, silicagel with pentane-dichloromethane, and silicagel with toluene. After the final concentration to 0.5 ml, the PAH's were determined by capillary GC with on column injection and FID detection.

Instrument: Carlo Erba 4160; Column: fused silica coated with SE-52 (d=0.32 mm; l=20 m); Carrier gas: helium (p=0.5 bar); Injector temperature: 80 °C; Oven temperature: 130 °C, programmed to 330 °C with 4 °C/min. Quantitation was carried out using a solution of anthracene in toluene as an external standard. GC/MS analyses were performed to confirm the identity of the PAH's.

Thermal Cleaning - Laboratory Experiments

Carefully weighed samples of 5-50 g were heated in a quartz tube in an electrically heated tube oven. The temperature, the residence time of the sample in the heated zone, and the composition of the atmosphere (air or nitrogen) were varied, and their

influence on the residual amount of total cyanide in the soil was measured. To obtain a cyanide balance, the gaseous decomposition products were collected by adsorption in a 1.25 M NaOH solution. This solution was used for a quantitative cyanide analysis after completion of the experiment. All experiments were performed in duplicate or triplicate.

Thermal Cleaning - Pilot Plant Experiments

Figure 1 gives a schematic drawing of the pilot plant used for the thermal cleaning of soils. The polluted soil is supplied to the rotating tube oven through a gas tight locking device. The tube oven is set at an inclination of 1.5 °C and is rotated at a speed of 4 rpm. The maximum input of polluted soil with a moisture content of 15 % is 500 kg/hr. Three oil or gas burners heat the tube oven to a maximum temperature of 850 °C. The gaseous decomposition products pass through a cyclone to remove dust and are then fed to an incinerator (temp. max. 1350 °C).

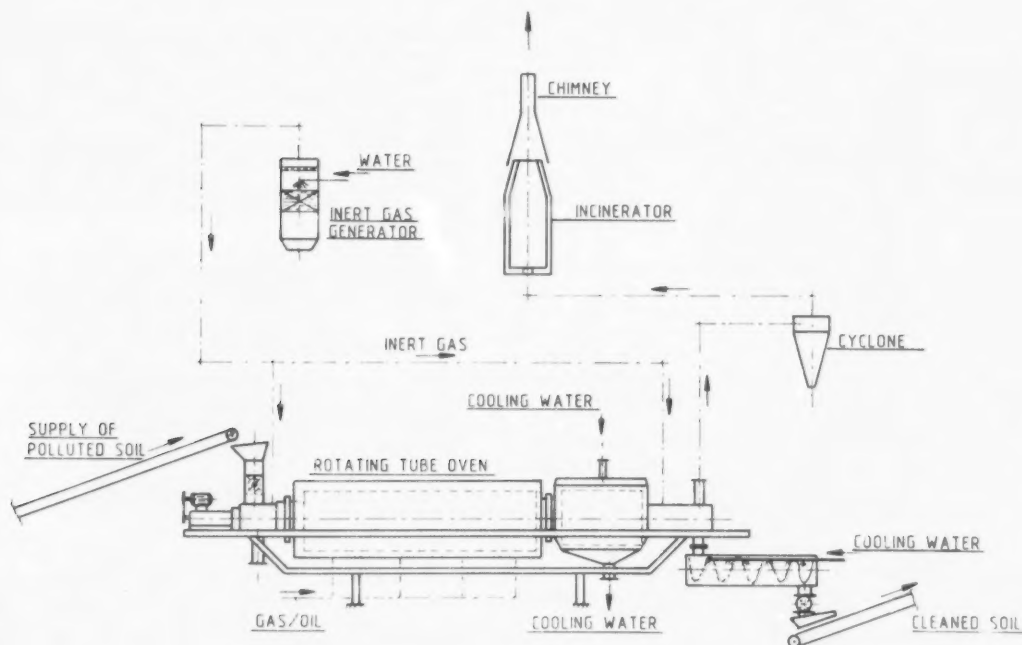


Figure 1. NBM pilot plant for the thermal cleaning of soils by indirect heating.

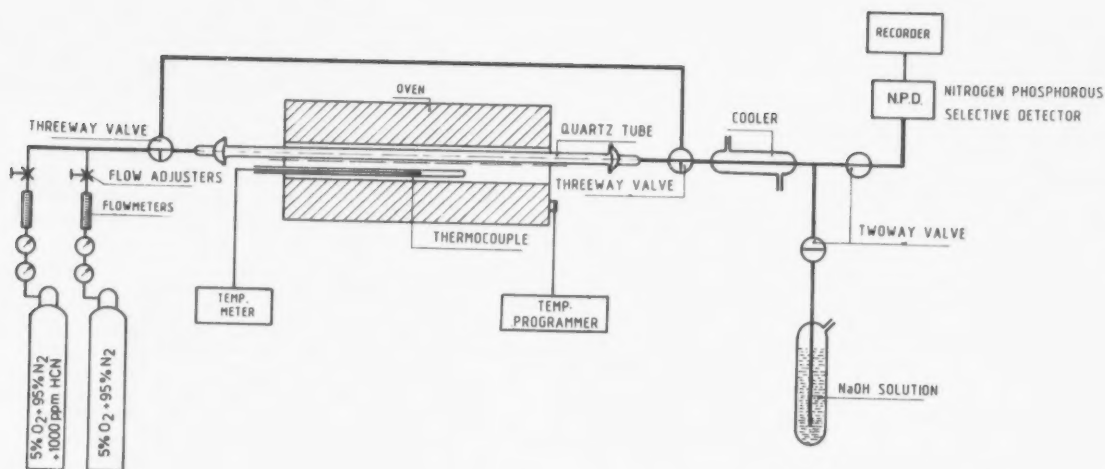


Figure 2. Laboratory installation for testing the incineration of HCN.

The cleaned soil leaves the tube oven through a gas tight locking device, is then cooled and moistened by spraying with water, and removed for storage. The tube oven, together with the input and output locking devices, are flushed with inert gas ($\text{CO}_2 + \text{N}_2$) to prevent explosions. The results of the study on the influence of the temperature of the tube oven and the incinerator on the residual amounts of cyanide on the soil and in the off-gas will be presented here.

Incineration of HCN - Laboratory Experiments

The incineration of HCN was studied in a quartz tube oven (Fig. 2) at temperatures of 800-1250 °C, residence times of 0.4-3.4 sec, and different oxygen concentrations. The concentration of HCN was measured by passing the gas stream through a NaOH solution followed by a colorimetric cyanide analysis or, directly by passing the gas

stream through a nitrogen-phosphorous selective detector (NPD) used in gas chromatography. This NPD shows a good linear response (5 decades) together with a high sensitivity ($10\text{E}-14$ g N/sec). In our experimental set up, the minimum detectable amount of HCN in the gas phase was $3.2 \times 10\text{E}-3$ ppm.

RESULTS

All three soils used had a sandy character and a low water content. The pH of soil B had a very low value, maybe due to microbiological conversion of sulfide to sulfuric acid. The results of the general characterization are given in Table 1.

First the influence of the temperature on the decomposition of the complex cyanides was studied. After heating for 1 hr at the given temperatures, the residual amount of cyanide in the soil was determined, together with the total amount of volatilised cyanides adsorbed in the NaOH solution. The results for soil C are given in Figure 3.

Table 1. Analytical results for the soil samples used in the thermal cleaning experiments.

Soil Sample	% dry weight	pH	Free CN (g/kg)	Total CN (g/kg)	Total PAH (mg/kg)
A	91	7.5	0.33	1.29	128
B	92	1.3	0.54	2.23	176
C	88	6.9	0.54	1.85	27

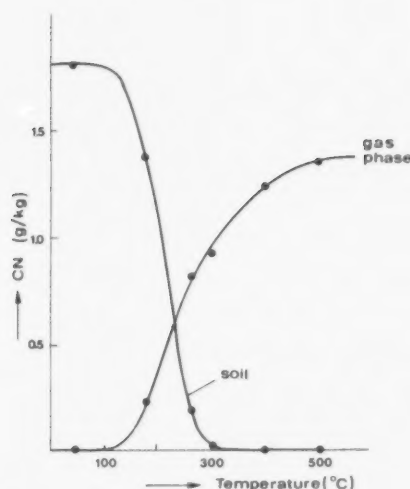


Figure 3.
Total amount of cyanide in the soil and the
gas phase after heating soil C for 1 hr.

Table 2. Influence of the contact time at 300 °C on the decomposition
of the complex cyanides in soil C.

Time (min)	0	10	20	30	60
Residual CN in soil (g/kg)	1.85	0.043	0.022	0.017	0.014

Table 3. The decomposition of complex cyanides on three soils at
300 °C and a contact time of 30 min.

Soil	A	B	C
CN in gas phase (g/kg)	0.56	1.17	0.88
Residual CN in soil (g/kg)	0.013	0.003	0.017
Total CN after heating (g/kg)	0.57	1.17	0.90
Total CN before heating (g/kg)	1.29	2.23	1.85

The influence of the residence time in the heated zone was studied with soil C at 300 °C. The results are given in Table 2.

A temperature of 300 °C and a contact time of 30 min was used to study the decomposition of the complex cyanides in the other soils. The results are presented in Table 3.

The results for the PAH analyses in the original samples and in sample A after heating for 30 min. at 300°C and 500°C are presented in Table 4. Heating of samples B and C gave identical results as for sample A.

Measurements performed during a 4 days experiment in the NBM pilot plant gave similar results. The wall temperature of the rotating tube oven was varied between 400°C and 650°C (soil temperature at exit approximately 100°C below wall temperature) with a load of 500 kg/hr. The soil was sampled at the entrance and the exit of the oven and analysed for total cyanide (Table 5).

Cyanide concentrations were also determined in the dust formed during the heating process, which is collected in the cyclone ($\pm$ 1% of the input). With a wall temperature of 550-650°C the cyanide concentration varied between 10-32 mg/kg, whereas at a wall temperature of 400°C the concentration varied between 98-755 mg/kg.

The results for the incineration of the HCN containing gas are not given in full detail, but exemplified with the decomposition of HCN in the laboratory experiments. Figure 4 gives the residual HCN concentration in the off-gas at different oven temperatures and flow rates. The initial HCN concentration was 326 ppm (0°C, 1 bar). The flow rate was kept constant while the temperature of the oven was varied between 750-1250°C.

Table 4.

Type of PAH	A	B	C	A300	A500
Phenanthrene	8	1.2	14	<0.01	<0.01
Anthracene	1	<0.5	2	<0.01	<0.01
Fluoranthene	22	5.3	33	<0.01	<0.01
Pyrene	27	<0.01	5.0	<0.01	<0.01
Benz[a]anthracene	9	2.3	11	<0.01	<0.01
Chrysene	12	3.7	15	<0.01	<0.01
Benzofluoranthene isomer	26	4.9	32	<0.01	<0.01
Benzofluoranthene isomer	2	<0.5	4	<0.01	<0.01
Benzo[a]pyrene	12	2.4	16	<0.01	<0.01
Benzo[e]pyrene	13	2.1	17	<0.01	<0.01
Perylene	4	0.5	5	<0.01	<0.01
Total PAH	128	27.4	176	N.D.	N.D.

Depending on the flow rate and the temperature, the contact time varied between 2.5 sec (30 ml/min at 800°C) and 0.4 sec (116 ml/min at 1200°C).

The influence of the oxygen concentration on the incineration of HCN is given in Fig.5.

In the pilot plant experiments incineration temperatures of 1100-1200°C were used. With a contact time of 0.5 sec, no cyanide could be detected in the flue gasses (detection limit 6 µg/m³).

DISCUSSION

The results presented in Fig.3 and Table 3 and 4 show that the indirect heating of soils contaminated with complex cyanides and PAH's is a very effective cleaning process. The percentage of cyanide removal after heating for 30 min at 300°C was 99.0, 99.9 and 99.1% respectively for the three types of soil used. PAH's were also removed under these conditions as their concentration decreased to below the detection limit (0.01 mg/kg).

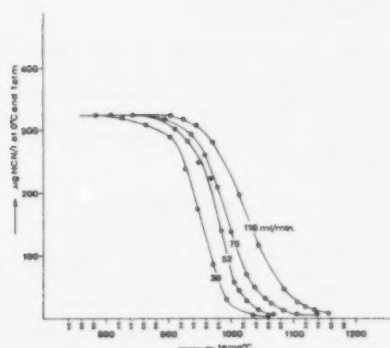


Figure 4.

Influence of the flow rate on the decomposition of HCN at different temperatures.

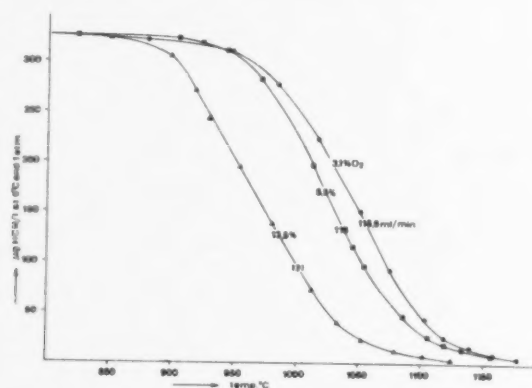


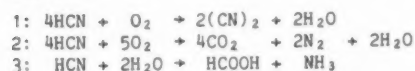
Figure 5.

Influence of the O₂-concentration on the decomposition of HCN at different temperatures. Contact time: 0.5 sec at 1000°C.

A large deficit in the cyanide balance is remarkable in these experiments (Fig. 3, Table 3). At 300°C only about 50% of the original cyanide was recovered from the gas phase. As the recovery of cyanide from the gas phase was shown to be quantitative and no cyanide remained in the soil, some unidentified chemical conversion of cyanide must occur.

Several assumptions can be made:

a). The complex cyanides decompose into HCN, followed by oxidation of HCN to $(CN)_2$ or CO_2 , or by hydrolysis to formic acid



b). The complex cyanides decompose into cyanogen $(CN)_2$.

Oxidation reactions can be excluded as they start only at about 800 °C and the same cyanide deficit was found when the reactions were performed in an inert (N_2) gas atmosphere. For the gas phase hydrolysis of HCN an increased conversion with increasing temperature should be expected, which was not observed.

Cyanogen formation may explain the cyanide deficit as $(CN)_2$ reacts with NaOH to give cyanide and cyanate, so only 50% of the



original cyanide is recovered in the analytical procedure. Assuming that the complex cyanides decompose into HCN or $(CN)_2$ the percentage of $(CN)_2$ in the gas phase can be calculated (Fig. 6).

Apparently, 100% of $(CN)_2$ is formed below 300 °C, while at higher temperatures mixtures of HCN and $(CN)_2$ must be formed. Possibly, the $(CN)_2$ reacts with hydrogen donors like H_2S or H_2O at high temperatures to form HCN. The cyanogen hypothesis was confirmed in one experiment by hydrolysing the cyanate to ammonia. Determination of the ammonia content gave the missing cyanide.

As expected from the laboratory experiments the indirect thermal treatment of cyanide soils presented no special problems in the pilot plant experiments. Above 400°C no significant influence of the temperature on the residual cyanide concentrations in the soil was detected. At a wall temperature of 400°C the residual cyanide concentration was 4.0 ± 1.3 mg/kg, but this value increased rapidly to 22 mg/kg when the temperature of the soil at the exit of the tube oven decreased to 225°C.

The cyanide concentrations in the dust formed during the heating process also increased considerably at temperatures below 400°C, indicating that the temperature was too low for complete conversion of the complex cyanides.

Incineration of HCN presented no special problems, both in the laboratory and the pilot plant experiments. A temperature of 1000-1200°C is sufficient for > 99.5% conversion. A high oxygen content in the incinerator gas is important as this may lower the incineration temperature necessary for > 99.5% conversion with ca. 100°C.

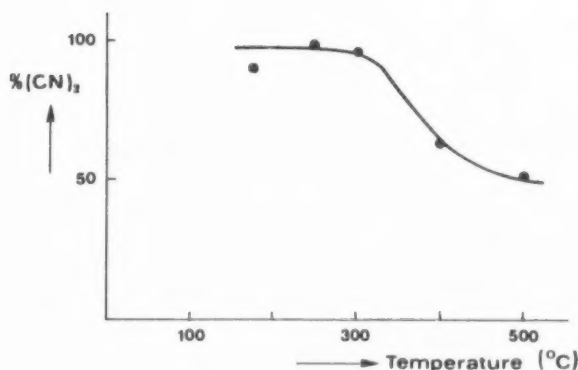


Figure 6.
% $(CN)_2$ in the gas phase after heating of sample C.

Table 5. Total cyanide in soil from a coal gasification plant before and after thermal treatment in a 500 kg/hr pilot plant. The average concentration (x), the standard deviation (s.d.) and number of determinations (n) are given for the input and output.

Wall temp. . (° C)	Total CN concentration in soil (mg/kg)					
	Input			Output		
	x	s.d.	n	x	s.d.	n
400	44	4	8	4.0	1.3	4
550	64	21	8	1.6	0.4	9
650	126	77	8	3.1	0.1	9
650	48	8	9	2.5	0.5	7

CONCLUSIONS

It was shown that soils, contaminated with complex cyanides and PAH's can be cleaned very efficiently by indirect heating in an inert gas atmosphere.

Pilot plant experiments on a 500 kg/hr scale have indicated that residual cyanide concentrations of ca. 2 mg/kg can be attained at a wall temperature of the rotating tube oven above 400°C.

Incineration of the HCN and (CN)₂ formed presents no special problems at temperatures above 1000°C.

The scaling-up of the present installation to a 20.000 kg/hr plant is under investigation.

ACKNOWLEDGEMENTS

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CLAY LINERS: WHERE DO WE GO FROM HERE?

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ABSTRACT

The use of clay liners as the sole liner for hazardous waste impoundments and landfills has declined substantially in the last several years. Questions have been raised about the effectiveness of clay liners and about the degradation of clay liners that are exposed to chemical wastes.

Clay liners do have an important place in land disposal technology, but many improvements are needed in design and construction technologies. More data are needed to confirm field performance. Monitoring of underlying aquifers is useful for determining whether major leaks have occurred but is of limited use in demonstrating that clay liners are performing effectively. Until earth scientists and engineers build a data base that demonstrates that clay liners are performing well, doubts about the effectiveness of clay liners will persist.

INTRODUCTION

Earth liners have been used worldwide for several decades to retard the movement of pollutant-laden liquids into the ground. Earth liners may be constructed from naturally-occurring clay soils or from mixtures of soil with bentonite. Such liners are often referred to as "clay liners" even though the earth liner is composed of less than 50% clay because the clay fraction controls the hydraulic properties of the liner.

Up until the late 1970's and early 1980's, the consensus among ground-water specialists seemed to be that clay liners were working fairly well. However, beginning in the early 1980's, a number of revelations raised questions about the

effectiveness of clay liners. In 1981, Brown and Anderson reported findings from EPA-sponsored research which showed that under laboratory conditions concentrated organic chemicals attack compacted clay and increase the permeability of compacted clay by several orders of magnitude. The organic chemicals rendered the clay essentially useless as a barrier to pollutant migration. Additional field work on prototype clay liners verified the earlier laboratory findings (Brown, Green, & Thomas, 1984).

The reputation of clay liners was further diminished when Daniel (1984) published an analysis of several case histories in which the

actual permeability of full-sized clay liners for water retention structures was determined from data on field performance. The liners were remarkably permeable despite the fact that laboratory permeability tests had indicated very low permeabilities. Because evaluations of nearly all existing clay liners for hazardous waste disposal facilities are based on results of laboratory permeability tests, it is possible that many more clay liners are leaking at rates far exceeding expectations.

Shortly after these and other findings were made public, the U.S. EPA changed its regulations in a manner that discouraged the use of clay liners for hazardous waste landfills. The initial set of regulations effectively banned the use of clay liners for hazardous waste landfills and impoundments. The current draft EPA regulations permit the use of clay liners, but only in a backup role to flexible membrane liners. In effect, these regulations reflect a low degree of confidence that clay liners can by themselves be effective in preventing the subsurface migration of pollutants from waste disposal facilities.

These facts raise questions about the future of clay liners. Will there be a continued decline in the use of clay liners and perhaps an eventual phasing out of clay liners altogether, or is it premature to assume that clay liners will be replaced by other technologies? The purpose of this paper is to examine the future of clay liners. Indeed, if clay liners do have a future, what needs to be done to solidify their place in the array of available containment technologies?

CAN CLAY LINERS BE EFFECTIVE?

Effectiveness as a Hydraulic Barrier

It would seem that one ought to be able to construct a clay liner that is reasonably effective in virtually stopping migration of liquids through the liner. After all, under laboratory conditions it is not particularly difficult to construct compacted clay liners that are almost impermeable to water. Typically, properly constructed compacted clays have permeabilities in the laboratory in the range of 1×10^{-8} to 1×10^{-10} cm/sec (Lambe, 1954; Mitchell et al., 1965; and Boynton and Daniel, 1985). With this range of permeability, a unit hydraulic gradient, and an effective porosity of 0.2, the velocity of water movement through a clay liner would range from 0.16 mm/yr to 16 mm/yr. Such rates of movement are so slow that molecular diffusion is probably a more important mechanism of pollutant transport than advective transport (Gillham et al., 1984).

Other mechanisms may tend to slow the rate of pollutant transport even more. For example, ion exchange, adsorption, precipitation, oxidation/reduction reactions, and biological degradation all serve to retard pollutant transport through earth materials.

The types of calculations and assessments presented in the previous two paragraphs are not new. These facts have been known for several decades and have formed the basis for a high degree of confidence among earth scientists and engineers that clay soil materials would indeed be effective in retarding the flow of both water and pollutants through such materials. Numerous laboratory experiments have served to confirm that rates of flow indeed can be quite small.

While it is clear that practically impermeable clay liners can be constructed in the laboratory, it is not clear that equally effective barriers can be constructed in the field. For example, Day and Daniel (1985) describe two prototype clay liners that were constructed in the field on EPA-sponsored research. The actual permeabilities of the liners were determined by ponding water on the liners for several weeks and measuring the rate of seepage. The permeabilities turned out to be only slightly less than 1×10^{-5} cm/sec despite the fact that laboratory measurements yielded permeabilities of 1×10^{-8} cm/sec or less. Day and Daniel concluded that hydraulic defects were present in the field that were absent from laboratory test specimens.

While it would seem that clay liners can be extremely effective as hydraulic barriers, there is no definitive base of field performance records to prove that clay liners are effective. The only reasonably well-documented cases of successful performance of clay liners were recently reported by Gordon et al. (1984). The cases involved 5-ft-thick clay liners beneath municipal waste landfills. Unsaturated zone monitoring beneath the liners showed that contaminants had not migrated significant distances in 5 to 10 years of operation.

Until more data of this type are developed, doubts about the effectiveness of clay liners are likely to persist. In addition, it is not clear that the hydraulic integrity of earth liners will be maintained during prolonged exposure to a myriad of concentrated chemical wastes.

Attack by Chemical Wastes

A number of studies have been conducted in the laboratory to evaluate the effects of chemical wastes upon earth materials. The tests show that concentrated acids can dissolve earth materials and lead to increases in permeability; however, earth materials have a large buffering capacity, and it may take large quantities of acid to produce sufficient dissolution of earth materials to yield a significant increase in permeability (Nasiatka et al., 1981; and Peterson et al., 1985).

Concentrated organic chemicals have been shown to cause large increases in the permeability of compacted clay even with small quantities of flow (Brown and Anderson, 1983; Brown, Green, and Thomas, 1983; Brown, Thomas and Green, 1984; and Foreman and Daniel, 1984). The data plotted in Fig. 1 are typical. Organic chemicals tend to flocculate clays and to cause other structural alterations, such as cracking, that lead to an increase in permeability. However, additional laboratory investigations have shown that effects of a particular chemical upon the permeability of a particular soil are strongly dependent upon the method of laboratory testing. Up to two orders of magnitude of difference in permeability have been observed between permeabilities measured in different types of permeameters on the same soils using concentrated organic chemicals (Hamidon, 1984). The overburden pressure applied to a clay also affects the susceptibility of the clay to attack by concentrated organic chemicals (Fig. 2) in laboratory experiments. Even the details of soil compaction can have a major effect on test results. In unpublished work at the University of Texas, identical soils were

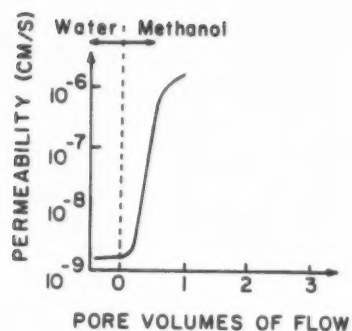


Fig. 1 Permeability of Compacted Clay to Water and Methanol (after Brown & Anderson, 1983)

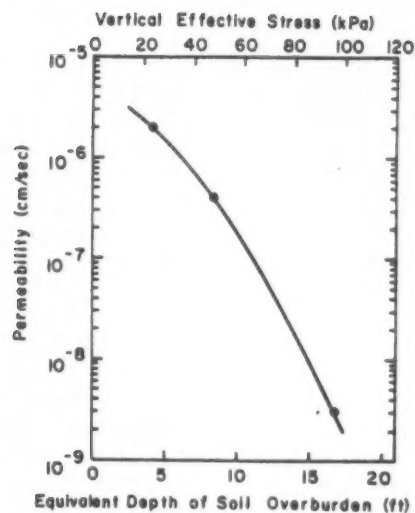


Fig. 2 Effect of Overburden Pressure on the Permeability of Compacted Clay that is Permeated with Methanol (Daniel, 1985)

compacted with two different ASTM compaction procedures (ASTM D-698 and D-1557) and then the soils were permeated with heptane. After 1 month of permeation, the permeabilities differed by a factor of more than 1 million. Thus, the effects of concentrated organic chemicals on clay materials depend very much on the details of testing. Because none of the laboratory testing techniques presently available exactly duplicates field conditions, one cannot be certain that the laboratory findings can be applied directly to field problems. Until this question is resolved, the effects of concentrated organic chemicals on the integrity of clay liners will remain a controversial issue.

Dilute organic chemicals do not seem to attack clay or to cause significant increases in permeability (Brown et al., 1984; and Daniel and Liljestrand, 1984). The data cited above show that certain chemicals can attack earth liner materials whereas other chemicals present no problem. If clay liners are to have a future, greater efforts are needed to minimize the possibility that clay liners will come into contact with liquids that could degrade the chemical and structural integrity of the clay liner.

HOW SHOULD CLAY LINERS BE DESIGNED AND CONSTRUCTED?

It is this writer's opinion that new directions are needed in the procedures used to design and construct clay liners if effective liners are to be achieved. The following recommendations provide a foundation:

1. Current design practice relies on the use of laboratory permea-

bility tests as an indicator of probable performance of a clay liner. The studies discussed earlier suggest that laboratory permeability tests can yield misleading values of permeability. It would be best, as part of the design phase, to construct a field test section using actual liner materials, full-sized construction equipment, and the actual construction procedures that are contemplated for the clay liner. Extensive testing could be done on the field test section to establish the actual permeability of the field-constructed clay and to evaluate other pertinent parameters. Such field data would provide far greater assurance that the clay liner will perform as intended than presently exists with current design methodologies.

2. The primary use of laboratory permeability tests should be to study the effects of chemicals upon the integrity of the clay liner. Use of field tests with water, supplemented by laboratory tests with chemicals, is the recommended approach. Because different types of laboratory permeability tests provide radically different results in some instances, more than one type of test may be needed. In addition, other types of tests besides just permeability tests should be performed (Bowders et al., 1985).
3. Construction practices for compacted clay liners have sometimes been inadequate. The presence of clods of clay may be very detrimental to clay liner performance (Daniel, 1984) so clods should be pulverized or otherwise

broken down prior to compaction of clay. The water content of the clay at the time of compaction is also important, but little attention is presently given to allowing time for the proper hydration of clay clods after water has been added to clay, but before the clay is compacted. Techniques for eliminating desiccation cracking during and after construction need to be developed. It may be necessary to cover the compacted surface immediately after construction, even if only temporarily. Construction techniques that lead to proper remolding and elimination of hydraulic defects during construction have received only superficial study so far. With greater recognition of the potential problems in achieving a clay liner with low permeability, and with greater attention to details of construction, it should be possible to achieve a much better product than is often seen today.

4. In laboratory tests, increasing the overburden pressure on clay reduces the susceptibility of clay to attack by chemicals (Fig. 2) and helps to close any cracks (Boynton and Daniel, 1985). The overburden pressure can be increased on the clay liner by increasing the thickness the thickness of the clay, placing solid material over the clay (such as loosely placed earth) that provides weight, or by placing solid waste over the clay in a way that spreads the load from the waste uniformly over the clay. At present, little consideration is given to the overburden pressure acting on a clay liner.

5. At present, too much emphasis is placed upon the permeability of a clay liner and too little emphasis is placed upon the overall impact of the liner on long-term pollution patterns. The real question should be: how rapidly will pollutants move through a clay liner, what will the nature of the effluent be, and what are the environmental consequences of leakage? Even the best of liners (clay or otherwise) are likely to develop leaks eventually, and an overall evaluation of that inevitable leakage is often overlooked.

WHAT ASSURANCES CAN BE PROVIDED THAT CLAY LINERS WILL PERFORM AS INTENDED?

At present very little is being done to verify that clay liners are performing as intended. Significant advances are needed in verifying the suitability of the as-built liner. Techniques are needed to measure the actual leakage rate through a clay liner. The current philosophy is to monitor aquifers beneath land disposal units for detection of massive leakage. However, this type of "negative" monitoring provides no usable data on those sites which are performing properly. Because the actual performance of liner systems is so critical, more detailed monitoring should be employed not only to detect leakage but also to verify the actual performance of the liner, be it good or bad. There are a number of ways in which this might be done, but little work has been initiated to apply monitoring technology for very slow rates of leakage through clay liners.

CONCLUSIONS

A common misconception is that clay liner technology is old and well

established. While it is true that clay liners have been used for many years, it is not true that clay liner technology is well established. In the next few years, there are likely to be substantial changes in the way clay liners are designed and built, and this should lead to the development of a sound, verifiable liner alternative. At present, the available data on field performance are so sparse that it is impossible to provide assurance that clay liners are always performing as intended. Clay liners may indeed turn out to have an important place in the future of waste disposal, but only if data are developed that lend confidence to this technology. The success of earth scientists and engineers in improving upon existing design, construction, and verification procedures, along with development of a data base that confirms the proper performance of clay liners, is the key to the future of clay liners.

ACKNOWLEDGMENTS

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THERMAL CONTRACTION AND CRACK FORMATION POTENTIAL IN SOIL LANDFILL COVERS

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ABSTRACT

Soil landfill covers in the northern states experience ground freezing to depths of 2 m or more. During periods of decreasing winter temperatures thermal contraction will increase tensile stresses creating the potential for crack formation. If elastic soil behavior is assumed, a drop of only 2 or 3°C will generate significant tensile stresses. Climatological data examined for three locations, along with computed ground temperatures, show larger drops in temperature. Frozen cover soils are comparatively weak in tension. Cracks, once initiated, propagating unstably through the frozen soil, may extend deeper than the tensile stresses to which they owe their growth. Simple elastic soil behavior used with thermal strains does not provide adequate information for prediction of thermal contraction and crack formation. Information is needed on the linear thermal contraction behavior of frozen soils, on the extent to which soil creep will reduce the tensile stresses, and on criteria suitable for preventing crack formation. Needed research may provide methods which are more economical than placement of additional cover soils to prevent freezing.

INTRODUCTION

Frozen soil landfill covers are subject to thermal contraction, increase in tensile stresses, and potential crack formation during periods of decreasing winter temperatures. These temperature conditions occur annually in the northern tier of states in the continental U.S. and most of Alaska. Potential cracking includes the full depth of freezing, 2+ m in some locations. Soil has a linear thermal coefficient of contraction almost five times higher than that of steel and a small decrease in temperature quickly generates tensile stresses. Because frozen ground is relatively weak in tension, initial fracturing commences at the ground surface and penetrates

the cover soils to the depth needed to relieve the tensile stresses. The cracks would be distributed over the cover surface in a pattern such that tensile stresses are reduced below the frozen soil tensile strength. These cracks normally would not be observed because they occur during winter cold periods, may be quickly covered with drifting snow, and may partially close with warmer ground temperatures.

The magnitude of winter temperature changes over short periods of time was determined by examining climatological records for 3 locations (Lansing, Michigan; Madison, Wisconsin; and Fargo, North Dakota). Ground temperatures were calculated at several soil depths as a function of time.

Based on elastic theory, tensile stresses were computed for the frozen soil using available soil thermal contraction coefficients and the temperature data. A comparison of these stresses with reported soil tensile strengths suggests that crack formation would be predicted for all three locations. The depth of crack formation will be dependent on soil type, temperature, water content, and any surface effects (vegetation, snow cover, etc.) which reduce the depth of freezing temperatures. Soil creep in tension during the period of decreasing soil temperatures will help reduce tensile stresses and crack depth. The results suggest that additional research is needed to provide soil parameters required for accurate prediction of tensile stresses and to provide design criteria suitable for preventing crack formation in soil landfill covers exposed to freezing temperatures.

BACKGROUND INFORMATION

Landfill covers designed to serve multiple functions will be layered in some fashion as illustrated in Figure 1. The top of a cover typically will be a loose, loamy soil suitable for supporting vegetation. The underlying clay barrier layer is a critical cover component because it is intended to minimize the transmission of water that would contribute to leachate generation and of gas that might kill vegetation and pose an explosion or other hazard. A buffer or foundation layer, sand or other soil, protects the barrier from damage. A buffer soil may also be placed above the clay barrier layer to increase depth in areas of deep frost penetration. Soil densities will correspond to those accomplished during spreading of cover soil with dozers and other compacting equipment. The topsoil is placed in

a loose condition and not compacted.

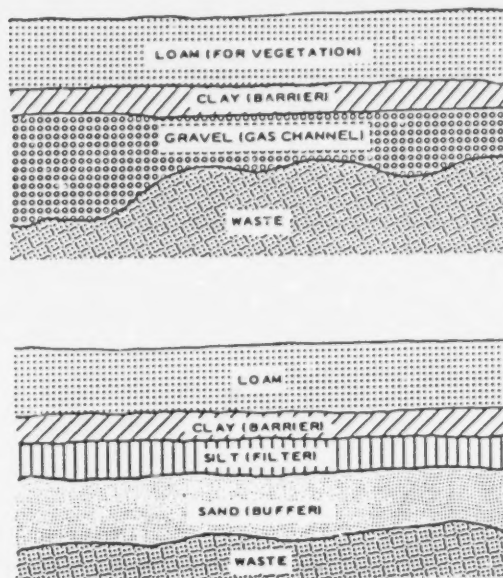


Figure 1. Two representative systems for layered solid waste(1).

Thermal contraction behavior and tensile strengths of frozen cover soils are dependent on several variables including soil type, ice and mineral volume fractions, temperature, and degree of ice saturation. The topsoil (loam) may involve several types (1) including silty gravels, clayey gravels, silty sands, clayey sands, inorganic silts, and inorganic clays. Above the water table these soils will be only partially saturated with the degree of saturation related primarily to particle size. Soil type and water content determine the ice fraction when frozen. An approximate relationship between effective grain size and degree of saturation for soils located above the water table in temperature zones with moderate rainfall is shown in Figure 2. The D_{10} particle size corresponds to 10 percent of the sample finer by weight. The loam topsoils listed by Lutton (1), with degrees of saturation

intermediate to sand and silt, will have reduced frozen tensile strengths. The clay barrier layer will be close to or at full saturation with large unfrozen water contents. Other factors involved in the tensile behavior of frozen soils will be outlined later.

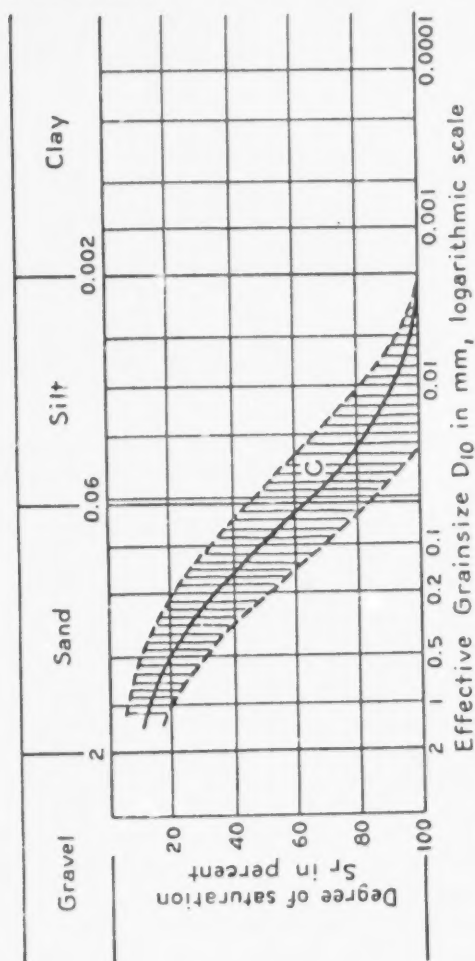


Figure 2. Approximate relationship between effective grain size and degree of saturation in the zone of soil moisture in temperate zones with moderate rainfall (2).

SURFACE AND GROUND TEMPERATURES

Ground temperatures are determined by the air (or surface) temperatures, heat flow from the interior of the earth, and soil thermal properties. Surface temperatures undergo approximately simple periodic fluctuations (Figure 3a) on both a daily and an annual cycle. Meteorological data for a given location are used to provide the mean annual temperature (T_m) and the surface temperature amplitude (A_s). The ground surface temperature ($T_{(s,t)}$) can be reasonably estimated as a sinusoidal fluctuation which repeats itself daily and annually, thus

$$T_{(s,t)} = T_m + A_s \sin\left(\frac{2\pi t}{p}\right) \quad (1)$$

where t is time and p is the period, 24 hours or 365 days. This temperature pattern is attenuated with depth (x) and, in a homogenous soil with no change of state, the temperature ($T_{(x,t)}$) at any depth can be calculated as

$$T_{(x,t)} = T_m + A_s \exp\left(-x \sqrt{\frac{\pi}{\alpha p}}\right) \sin\left(\frac{2\pi t}{p} - x \sqrt{\frac{\pi}{\alpha p}}\right) \quad (2)$$

where α is the soil thermal diffusivity and heat flow from the interior of the earth is assumed to be negligible. The simple solution represented by equation (2) indicates the trends found in actual ground temperatures but, in practice, they can be significantly modified by the effects of latent heat, differences in frozen and thawed soil thermal properties, non-homogenous soils, non-symmetrical surface temperatures because of seasonal snow cover, vegetation, and other climatic influences.

Thermal contraction and development of tensile stresses in the frozen

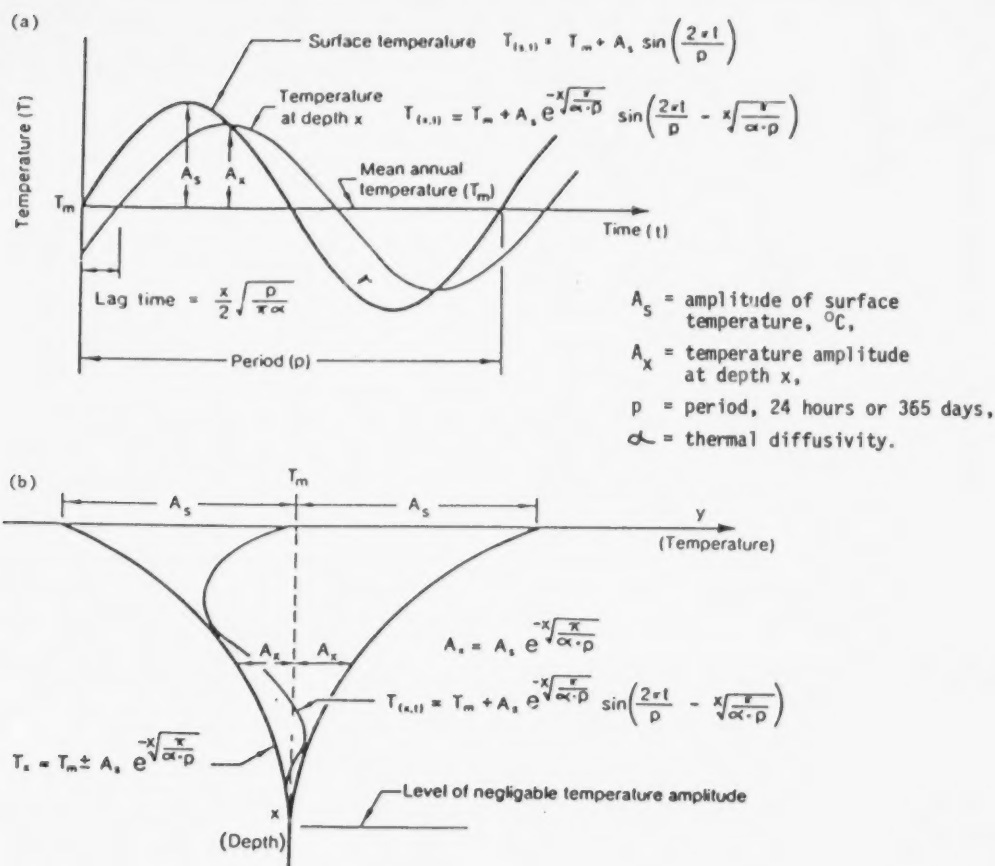


Figure 3. Surface and ground temperatures (3). (a) Sinusoidal fluctuations. (b) Temperature attenuation with depth.

soil cover will be most critical during a period of relatively rapid decrease in temperature. To determine the magnitude of these temperature changes climatological records for 3 locations (Lansing, Michigan; Madison, Wisconsin; and Fargo, North Dakota) have been examined with selected data summarized in Figure 4. These data may not include the largest negative temperature gradients since only a partial examination of the available temperature records was made. The record temperature

drop experienced by large areas of the central U.S. on the night of January 20, 1985, may be more severe than the data reported in Figure 4. Variations in temperature from the sine curve shown in Figure 3 are a result of winter weather changes. Note that at all three locations the freezing temperatures decreased more than 15°C in a 12 hour period. Colder temperatures at Madison, Wisconsin, and at Fargo, North Dakota, would penetrate the soil cover to a greater depth, hence more frost penetration.

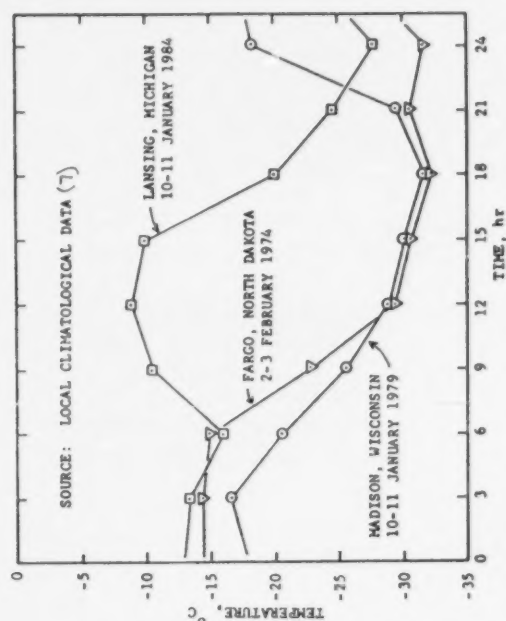


Figure 4. Selected air temperatures at three locations showing a rapid decrease over a 24-hour period.

The depth of ground freezing (frost penetration) can be calculated using the local freezing index and soil thermal properties. The freezing index is defined as the cumulative degree-days (below 0°C) for one winter season and corresponds to the area between the 0°C line and the negative part of the surface temperature curve in Figure 3a. The modified Berggren equation (4) accounts for phase change and gives the frost penetration in terms of the soil thermal conductivity, the ground surface freezing index, and soil latent heats. For comparative purposes, the computed maximum frost depths for each location and year included on Figure 4 are listed in Table 1 for three soil types. The frost depths at each site listed in Table 1 can be larger since the

Table 1. Maximum frost depths for the three locations during the year (Figure 4) for sand, silt, and clay soils.

Location	Frost depth, cm		
	Sand $\gamma_d = 15.0 \text{ kN/m}^3$ $w = 8.3 \%$ $S = 30.0 \%$	Silt $\gamma_d = 14.0 \text{ kN/m}^3$ $w = 26.2 \%$ $S = 80.0 \%$	Clay $\gamma_d = 16.0 \text{ kN/m}^3$ $w = 24.2 \%$ $S = 100 \%$
Fargo, North Dakota, 1973-74	210	155	196
Madison, Wisconsin, 1978-79	162	110	133
Lansing, Michigan, 1983-84	115	83	100

γ_d = soil density (kN/m^3), w = water content (% dry weight basis), and S = degree of soil saturation (% average from Figure 2). The ground surface was assumed to have no snow or turf cover.

coldest year (largest freezing index) may not have been used in calculations. Selected dry densities and degree of saturation included in Table 1 would be representative of

the cover topsoils and the clay barrier layer. Note that the greater frost depth corresponds to sand with a lower water content. The potential for cracking includes the full frozen soil depth.

Frozen soils behave elastically in response to rapid deformations. If one assumes the same behavior for the slower natural thermal contraction, the tensile stresses generated would be proportional to the amount that the temperature drops from some reference temperature. To provide more information on the rate of temperature drop at various depths, computed temperatures in clay are summarized in Figure 5 for Fargo, North Dakota, on 2-3 February 1974. Using a step change in surface temperature and the LaPlace-transform technique (5), soil temperatures were computed as a function of time at the depths shown in Figure 5. The zero depth represents the ground surface. Lachenbruch (6) reported that significant tensile stresses would be generated in frozen soil with a temperature drop of only 2 to 3°C. The temperature change in 9 hours at the 24 cm depth falls in this category. With more time, similar temperature changes would occur at greater depths.

THERMAL CONTRACTION, TENSILE STRESSES, AND SOIL STRENGTH

On cooling, the frozen soil cover surface would contract if it were not constrained. Horizontal tensile stresses are generated with no observable horizontal strains. The horizontal thermal strain is given by the thermal contraction, thus,

$$\epsilon_y = \epsilon_z = \frac{\Delta L}{L_0} = \alpha \Delta T \quad (3)$$

where α is the coefficient of linear contraction (about $5 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$ for

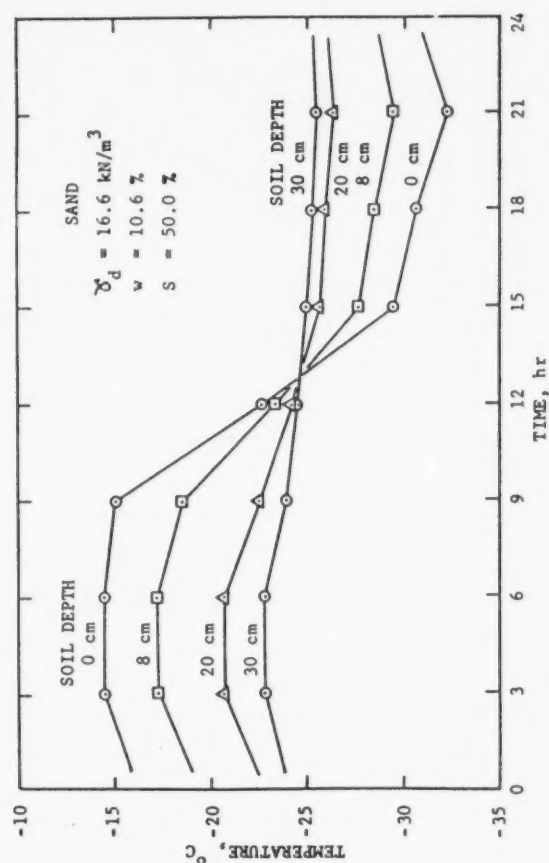


Figure 5. Computed ground temperatures in sand for Fargo, North Dakota, on 2-3 February, 1974.

frozen sand), L_0 is the length at some reference temperature, and ΔL is the change in length due to a temperature change ΔT . With the soil constrained and if the frozen soil is assumed to behave elastically the tensile stress becomes

$$\sigma_y = \frac{E}{1-\mu} \epsilon_y = \frac{E}{1-\mu} \alpha \Delta T \quad (4)$$

where E is Young's modulus and μ is Poisson's ratio. The stress-strain curves for sand (Figure 6) in tension

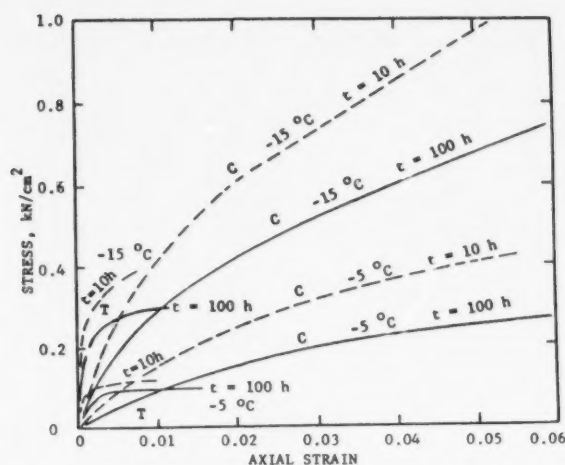


Figure 6. Stress-strain curves for frozen sand in compression (c) and tension (t) with test duration (t) in hours (8).

at -15°C gives an E close to 435 kN/cm^2 . Using this value with $\mu = 0.28$ gives $\frac{E}{1-\mu} \approx 600 \text{ kN/cm}^2$ or $\sigma_y \approx 0.03 T (\text{kN/cm}^2)$ for equation (4). The tensile strength of the saturated frozen sand in Figure 6 is at most only 0.4 kN/cm^2 indicating that frozen sand will be very sensitive to a temperature decrease. Note that failure stresses in tension are much smaller (Figure 6). With only partial saturation for frozen cover soils, tensile strengths would be further reduced since only the ice matrix is able to transfer tensile stresses. Considering the data summarized in Figure 5 and assuming elastic soil behavior, the frozen soils would be close to failure in tension before the rapid air temperature drop occurs. The additional temperature decrease shown in Figure 5 would cause additional thermal contraction and larger tensile stresses. The total tensile stress would then be significantly greater

than the tensile strength of the frozen saturated sand and open cracks would be predicted. For the given assumptions Lachenbruch (6) states that the crack spacing would be no greater than the crack depths.

The example with sand illustrates that simple elastic behavior does not fully represent the frozen soil behavior. Frozen soil under a constant stress will deform with time in a viscous manner. This creep behavior would serve to reduce the tensile stresses over the period of time in which temperature is decreasing. If a viscous deformation law is assumed the stress would be proportional to the rate at which the temperature drops. The rate of temperature decrease at various soil depths is represented by slopes of the curves in Figure 5. The data in Figure 6 also show that Young's modulus increases with a decrease in temperature so that the problem becomes more complex. Experimental data are needed which describe the rate of increase and magnitude of tensile stresses which develop in typical cover soils for freezing temperatures and cooling rates representative of the northern tier of states. The lack of information on linear thermal contraction behavior for these same soils indicates additional research needs before an accurate analysis of thermal cracking in the cover soils can be made.

CONCLUSIONS

1. A review of the mechanics of thermal contraction indicates that cracks propagating unstably through the frozen cover soils may extend deeper than the tensile stresses to which they owe their growth. Under suitable conditions it appears that the cracks may penetrate the frozen cover creating an opening for water

movement and escape of gases.

2. Information on the linear thermal contraction behavior of frozen soils needed for computation of thermal strains is lacking. The dependence of the coefficient of linear contraction on various soil parameters should be determined.

3. Simple elastic soil behavior used with thermal strains does not provide the information needed for accurate prediction of thermal contraction and crack formation. Information is needed on the rate of increase and magnitude of tensile stresses which develop in frozen cover soils for freezing temperatures and cooling rates representative of the northern tier of states.

4. Using information from items 2 and 3, criteria need to be formulated which will permit prediction of cracking and the techniques suitable for preventing crack formation. New techniques may be more economical than placement of additional cover soils to prevent freezing and possible cracking of the clay barrier.

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SYNTHETIC LINER SELECTION AND APPLICATION TO GROUNDWATER PROTECTION

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ABSTRACT

This paper discusses the use of synthetic liners as a means of controlling groundwater pollution.

It discusses the most common types of raw materials for liners: chlorosulfonated polyethylene, polyvinyl chloride and polyethylenes, and other liner materials: butyl rubber, chlorinated polyethylene, ethylene propylene diene monomer and chloroprene.

The manufacturing processes are described for producing the final synthetic liner including calendering, blown film and sheet extrusion.

The various seaming methods for factory and field seaming are defined and include adhesive seams, extrusion, hot air, bodied solvent and solvent seams.

Causes of failure are presented such as chemical attack, puncture and tear, and biological. Also, the paper presents information on how to select a lining system for a particular application.

The emphasis throughout this paper is on specifications for all segments of the synthetic liner industry, and guidelines for the end user on how to determine if the product meets those specifications.

A flow chart for quality control and selection for various synthetic liners is presented.

Introduction

In recent years, the need for containment of hazardous wastes has received much attention as the potential dangers to public health from these substances receive closer scrutiny from both the public and private sector. This paper deals specifically with the use of extruded polymers as perhaps the most effective means of containing hazardous wastes. Also it describes some lining materials in use today, methods of manufacture and some common failure mechanisms.

Background and Materials Available

Throughout history, soils and clays have been the most common lining materials. These substances have never been considered perfect liners as they do not provide zero permeability. Since both organics and inorganics dissolve parts of clay structures, permeability usually increases over time.

Many polymeric materials will exhibit essentially a zero permeability rating when used in a film or sheet form. As a result,

these materials offer long-term containment possibilities for ground water protection. The first polymeric materials used for this purpose were synthetic rubbers in the 1940s. By the 1970s, many new synthetic lining materials, particularly thermoplastics, were available.

Today synthetic liners are used to contain hazardous wastes, protect groundwater and control erosion. There are a variety of applications and a variety of lining materials.

Liner Materials

The most commonly used base materials for synthetic liners are:

Chlorosulfonated polyethylene (CSPE), a polymer produced by reacting polyethylene in solution with chlorine and sulfur dioxide. CSPE contains 25 to 45 percent chlorine and 1.0 to 1.4 percent sulfur, both by weight. The presence of chlorine and sulfur side-chains in the end product has a noticeable effect on its chemical compatibility with hydrocarbons. CSPE exhibits poor resistance to both aliphatic and aromatic hydrocarbons, chlorinated solvents, oxygenated solvents and alcohols.

Polyvinyl chloride (PVC), a polymer produced by the polymerization of vinyl chloride monomers, with plasticizers added to improve flexibility. Because it also contains side-chains of chloride, it offers limited resistance to hydrocarbons. PVC blended with ethyl acetate also has side-chains.

Polyethylenes, because of their simple chemical structure, exhibit the best resistance to hydrocarbons, as well as to other chemicals. Laboratory tests have shown that the

higher the density, the greater the resistance to chemicals, including hydrocarbons.

Other, but less commonly used, base materials are:

Chlorinated polyethylene (CPE), produced by chemical reaction between chlorine and polyethylene. The resulting polymer is 25 to 45 percent chlorine by weight and contains side-chains of dissimilar members. CPE has excellent flexibility but limited resistance to hydrocarbon environments.

Ethylene propylene diene monomer (EPDM), a terpolymer of ethylene, propylene and a small amount of nonconjugated diene to furnish vulcanization sites. The material has good chemical resistance except with hydrocarbons.

Epichlorohydrin rubber, a synthetic rubber that includes two epichlorohydrin-based elastomers, which are saturated, high molecular weight, aliphatic polyethers with chloromethyl side-chains.

All of the above polymers mentioned have been successfully used in a variety of containment applications. However, some of them have also failed. These failures can be attributed to poor selection, poor installation and/or changes in the containment application at a later date.

Butyl rubber, elasticized polyolefin and polychloroprene are the least commonly used base materials.

In addition to base polymers, there are blends and combinations of the above which are used either alone or with other additives. These additives include: plasticizers for improved flexibility; crosslinking

agents for promoting the formation of chemical bonds; fillers to give body; pigments for coloring purposes; biological inhibitors to reduce susceptibility to attack by microorganisms; and scrim reinforcement for improved mechanical strength.

These additives are used to overcome an inherent weakness in a base material, but their use must also be suitable in contact with the contents of a containment system.

Manufacture of Synthetic Liners

Flexible membrane liners are produced into a film or sheet by one of three processes: blown film, calendering or sheet extrusion. In the blown film process, molten plastic is extruded through a tubular die in a vertical direction. Air is blown through the die to form a bubble. After the bubble is cooled from the outside, it is flattened at the top of its travel by a collapsing frame. The resultant film or sheet is then passed through a wind-up system. The blown film process is most commonly used to make thin polyethylene film, 10 to 30 mil in thickness. With this process the size of the sheets is limited. It must be noted as well that some blown-film liners contain a lubricant, typically calcium stearate, to facilitate extrusion through the circular die. This peculiarity of some blown-film liners must be taken into account when the seaming method is specified; a process that employs preheating will likely cause the lubricant to migrate to the surface and interfere with seam integrity. The collapse and wind-up process may also subject the liner to unacceptable tensile stressing.

Most lining materials are produced by the calendering process, with the exception of some of the

polyethylenes. Calendering is really a form of extrusion with rotating die nips. A typical operation contains four rolls forming three nips. The first is the feed pass, the second is the metering pass and the final nip is the sheet forming, gauging and finishing pass. The most typical liner width produced by calendering is five feet, although some calenders are 10 feet wide. Thickness of lining material produced by this process is generally limited to 10 to 60 mil.

With the sheet extrusion process, molten plastic is forced through a die to form the final width of sheets desired. Sheets made by the extrusion process can be made in thicknesses as great as 250 mil, although 80 to 100 mil is more typical. One manufacturer is able to extrude sheets that are 34 by up to 900 feet in length for few field seams.

It is important to consider what services the liner manufacturer will provide in addition to producing the liner panels. Figure I is a flow chart depicting the various functions that should be examined when considering a polymeric material.

In the majority of liner applications, site engineering work is done for the operator of the final facility by a consulting or in-house engineer who recommends the required amount of lining material to cover the application. The manufacturer in those cases only supplies the lining material. After manufacture, the liner is turned over to fabricators for finishing and factory seaming and then to installers, or contractors, who complete the project. Each party in this typical factory-to-field scheme is an independent firm.

When designing a secure containment application, numerous factors involved in the complete job should be considered, with particular attention to seaming methods, chemical resistance, puncture and tear resistance and resistance to biological attack.

Seams and Seaming Methods

All liners are seamed, either in the factory or the field or both. Because seams are the most obvious weak points of a lining system, they must meet all the specifications for the liner itself. Seaming methods include:

Adhesive seams are joined together with a chemical adhesive system that bonds together two separate membrane surfaces. Generally, a two-component system is employed that requires care in mixing. When the adhesive is applied, the residence time before bonding, pressure applied and timing of pressure are all critical. These variables may be difficult to control in a field situation.

With a bodied solvent seam, lining material is dissolved in a solvent used to soften and bond liner surfaces together. This method is essentially an adhesive seam made up of the parent material. Because problems with application, timing and pressure do exist and the amount of solvent used is critical, field application requires extreme care.

Dielectric seams are made when a high frequency current is used to melt the surfaces of the membrane material so that they can be homogeneously bonded together under pressure. This process is used most often for factory seams, because the use of high frequency current is difficult to control in the field.

For extrusion welded seams, a bond is obtained between two flexible membranes by extruding a molten ribbon of the parent material between overlapped pieces of liner material followed by applied pressure. This is a relatively straightforward task in the field.

Solvent seams use solvents to softens the surfaces to be bonded. Generally pressure is then applied to the seam. Under field conditions, the application of the solvent, and timing and pressure can be a difficult task.

A chemically adhesive tape seam may be used to bond liner surfaces together. The tape system adds an additional element to the seam system that must be assessed for the requirements of the application. Taped seams are commonly made in the field and are subject to all the hazards associated with adhesive seams. The adhesive is different material and must meet criteria and needs of application.

To make thermal or fused seams, high temperature air or gas is applied between the two surfaces to be bonded until the membrane surfaces melt. At that time pressure is applied to create a homogeneous bond between the two surfaces. Timing and pressure are critical and must be carefully controlled. The recent development of a process that grinds material from the bonding surfaces and incorporates it into the seam is, in this author's opinion, one to be avoided because of the risk of encapsulating sand or dirt particles. Foreign material within a seam likely signals a void.

Vulcanized seams are formed when the areas to be bonded are unvulcanized material that are cured together with heat and pressure. This method is applicable only for thermoset materials.

Chemical Resistance

The primary purpose of a synthetic liner is to protect groundwater from contamination. Obviously the liner itself must be resistant to the chemicals being contained. When considering chemical resistance, the operating temperature of an impoundment as well as the potential for exothermic chemical reactions must be taken into account. Whenever possible, chemical compatibility tests are recommended, even urged, to assure that a liner material is an appropriate one for the operating uses in question.

Puncture and Tear Resistance

It is impossible to overemphasize the importance of liner thickness to the integrity of the overall lining system. The puncture and tear resistance of a given plastic material is related directly to its thickness and approximates a geometric function. In tests to determine the relationship of high density polyethylene (HDPE) liner thickness to puncture resistance, DIN 16 727 describes a single point application of high physical stress at high deformation speed, a stressing mode that can occur easily at an installation site. Results showed that the height of fall from which no damage takes place triples when liner thickness is doubled, from 1.5mm to 3.0mm for example.

In tests of a HDPE liner for tear resistance in accordance with DIN 53 515, a Graves angle test specimen is subjected to tensile stressing at a

speed of 500mm (20in.) per minute. The test simulates rapid tearing as would likely be found in actual site conditions, and shows that as liner thickness is doubled, tear resistance also doubled.

Another critical aspect of specifying liner thickness is the ability of a given thickness to accommodate the almost inevitable subsoil settling that can be expected under most impoundments. The design engineer must ensure that the liner material is sufficiently strong and thick to withstand the multi-axial tensile loading and to alleviate localized stress points with sufficient elongation behavior.

Resistance to Biological Attack

A potential failure mechanism for lining systems and one that is often overlooked is biological attack. Any polymeric material containing plasticizers will likely be subjected to microbiological attack. Microbes actually consume certain organic plasticizers; as the plasticizer is lost, the liner becomes less flexible. Eventually it will become brittle and crack.

Small rodents and burrowing animals sometimes use a liner as a food source, even to the point of becoming addicted to certain plasticizers. Linings containing rodent food sources should not be specified for areas where rodent populations are known to be active. Rats can gnaw through a liner in unexpected locations making it difficult to isolate and repair any leaks.

Thin (60 mil or less) synthetic liners are also susceptible to penetration of roots and plant life through them. Soil sterilization is a distant alternative to the better

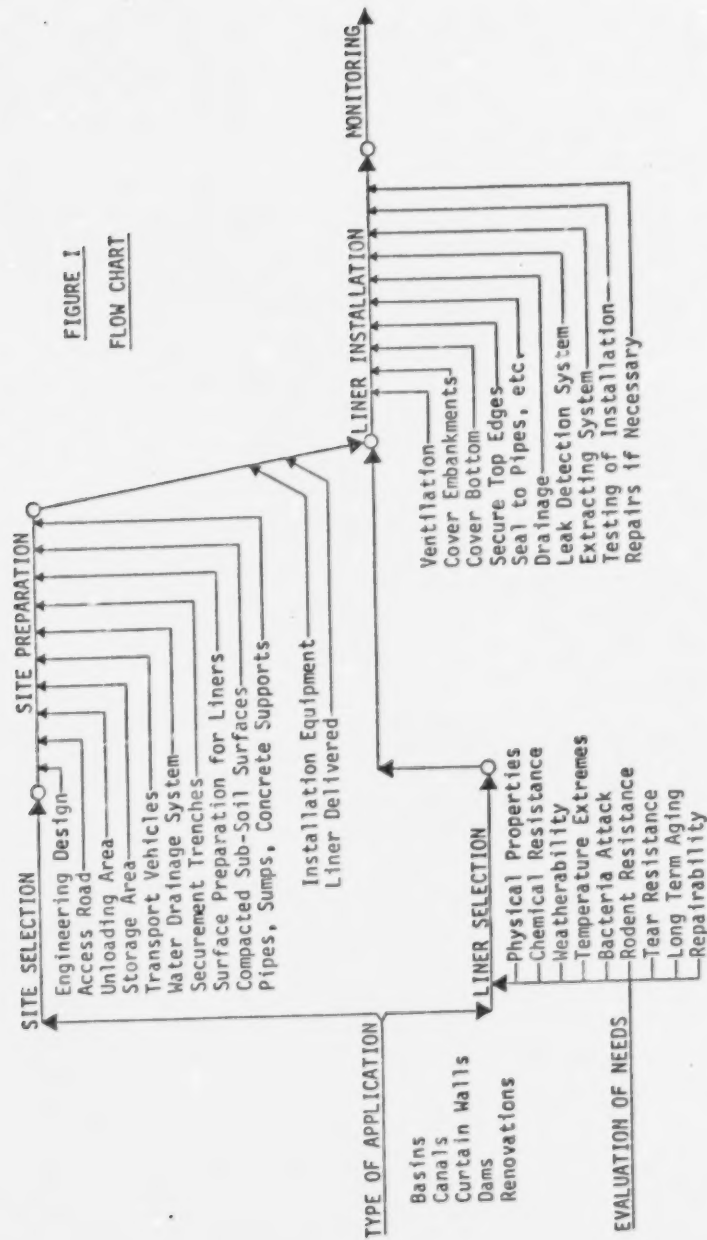
choice of specifying a thick liner that is impenetrable to such plant life.

Conclusion

The use of extruded polymers for the containment of hazardous wastes is a vitally important and beneficial use of plastic and rubber materials. The details that factor into a well thought-out specification, however, are numerous and sophisticated. This paper has highlighted some of the fundamental design and specification issues that must be considered so that a lining system services both the user and the public.

Disclaimer

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SLURRY WALL MATERIALS EVALUATION
TO PREVENT GROUNDWATER CONTAMINATION
FROM ORGANIC CONSTITUENTS

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ABSTRACT

The installation of earthen liners and slurry wall trenches constructed of soils treated with bentonite and/or bentonite/cement mixtures are frequently used today as a means to retard or control the flow of contaminants from surface impoundments and landfill disposal areas. Although effective in reducing the rate of flow of water and some contaminants, standard bentonite treatment is not always effective in controlling some types of contaminants, such as chlorinated hydrocarbons.

Past handling and disposal of liquid chlorinated hydrocarbon waste in earthen impoundments and a landfill at an existing plant resulted in shallow ground water and soil contamination over a broad area. Following field investigations, extensive laboratory tests were conducted to investigate the feasibility of confining the plume of contamination through the installation of a slurry trench barrier. Specially designed methods of testing were used during the investigation.

Standard bentonite soil mixtures using up to 6% or more bentonite were shown to be ineffective in restricting the flow of the concentrated wastes found in the subsurface strata. However, a 12%/12% bentonite/cement dust soil mixture was shown to completely restrict the flow or movement of the concentrated waste while reducing the flow of ground water and contaminated leachate.

INTRODUCTION AND PURPOSE

Bentonite, or more specifically the clay mineral montmorillonite, has been used for decades to impede or reduce the flow of water through permeable soils. This characteristic has been widely used in the drilling and construction industries.

The use of bentonite began in the petroleum exploration industry during the 1920's in drilling muds used to seal the sides of the hole and to provide other benefits which aided the drilling operation. During the 1940's, it was found that borings

and trenches could be kept open using a slurry of bentonite, and that the resulting trench when backfilled exhibited a reduced permeability to the horizontal flow of ground water. More recently, bentonite slurry wall trenches have found application to control pollution migration for improperly designed waste landfills and impoundments.

The design of soil bentonite slurry walls for conventional groundwater control applications has been widely documented. Other than

normal standard testing, very little investigative work is required. The design of a soil-bentonite slurry wall for waste containment however, requires site specific studies in order to determine the effectiveness of the proposed barrier.

APPROACH

Test Program

The presence of organic or inorganic compounds in the groundwater can have a detrimental effect on the bentonite slurry wall and its ability to contain contaminants. Certain chemicals can affect the chemical/physical properties of the bentonite and cause failure of the barrier either during construction or at some time in the future. Therefore, the effects of the groundwater, waste leachate or liquid waste on the soil/bentonite system must be determined prior to the preparation of final design specifications for the slurry wall.

Prior to the start of laboratory investigations, detailed field investigations are essential to determine the geohydrology of the proposed slurry trench site. Unless detailed information is available, sufficient soil borings should be made of the entire area to define the geology, particularly within the area in which the proposed trench will be located. In addition, sufficient pump tests and field permeability tests should be made to define the hydrology of the area.

During the course of the field investigations, chemical analysis should be made on the groundwater and core samples to define the extent of the contamination plume. Samples of soil, the waste, groundwater and leachate should be collected for use in subsequent laboratory evaluations of the proposed slurry trench composition.

In this paper, the authors describe the laboratory investigations conducted during the evaluation of a proposed slurry trench barrier to contain contamination from an existing industrial disposal area.

Site Description

The site for the proposed slurry trench barrier was an old disposal area within a large petrochemical manufacturing plant that had been used for various waste activities in the past. This included the collection and storage of liquid chlorinated hydrocarbon wastes in earthen pits or ponds and the landfill disposal of solid organic and inorganic wastes, drums of miscellaneous liquid organic wastes, plus construction debris such as wood, concrete, etc.

The field investigations indicated that extensive shallow groundwater and soil contamination had occurred. In addition, immiscible and relatively pure undiluted waste organics were found to exist at points more than 300 feet away from the original source and down to depths as great as 50-60 feet below the surface.

Site Geology

The geology of the area was characterized by a combination of hydraulic and mechanical fill overlying deposits of recent alluvium. Extensive geological investigations of the area were conducted and a detailed description of this area developed.

The proposed area where the slurry trench barrier would be constructed was on the eastern edge of the disposal area. Several core borings were drilled in this area.

The geology of the proposed slurry trench area was characterized

by several distinct layers of soil. The area is covered with a layer of silty clayey sand fill material from the surface to a depth of approximately 12 to 14 feet below the surface. Beneath this on the northern end of the proposed trench area is a soft black organic clay layer approximately 4 to 6 feet thick. Beneath this is a layer of fine to medium silty sand approximately 25 to 5 feet thick that extended downward to a depth of 50 to 60 feet below the surface. Underlying these soil layers is a stiff light gray to tan clay found at depths of 50 to 60 feet below the surface throughout the area. Electric logs of wells in the area indicate the thickness of this base clay layer to be 75 to 100 feet.

Samples of soil and groundwater taken from core borings show the soil and water in the area of the proposed slurry trench to be contaminated with chlorinated hydrocarbons. Data from samples show contamination was present at various depths down to the base clay encountered at a depth of 57 feet below the surface. Continuous samples were not taken for contamination analysis from all borings. However, a composite of samples taken at 2 feet intervals showed high levels of contamination. Visual evidence of high concentrations of phased organic contaminants was noticed during the drilling operation, especially at depths of approximately 12 through 20 feet below the surface. An composite analysis of samples taken at 2 feet intervals from the depths of 2 to 65 feet below the surface showed the soil contained 0.59 wt.% total chlorinated hydrocarbons. These results are presented on Table 1. Groundwater samples taken from the same location contain 942 ppm of total chlorinated hydrocarbons as shown on Table 2.

TABLE 1. CHEMICAL ANALYSIS OF COMPOSITE SOIL MIXTURE B

Compound	Wt.
Methyl Chloroform	0.02
Trichloroethylene	<0.01
Trichloroethane	0.03
Perchloroethane	0.04
Tetrachloroethane	0.01
Tetrachloroethane (Sym)	0.06
Pentachlorobutadiene	0.10
Hexachlorobutane	0.05
Hexachlorobutadiene	0.26
Unknown	0.02
Total	0.59

TABLE 2. GROUNDWATER ANALYSIS

Component	Concentration mg/l
Chloroethylene	0.80
Chloroethane	0.04
Methylene chloride	0.15
1,1 - Dichloroethene	25.9
1,1 - Dichloroethane	4.08
1,2 - Dichloroethene	--
Trichloromethane	513
1,2 - Dichloroethane	4.82
1,1,1, - Trichloroethane	4.82
Tetrachloromethane	--
Trichloroethene	7.12
1,1,2 - Trichloroethane	260
Tetrachloroethene	126
Total	942

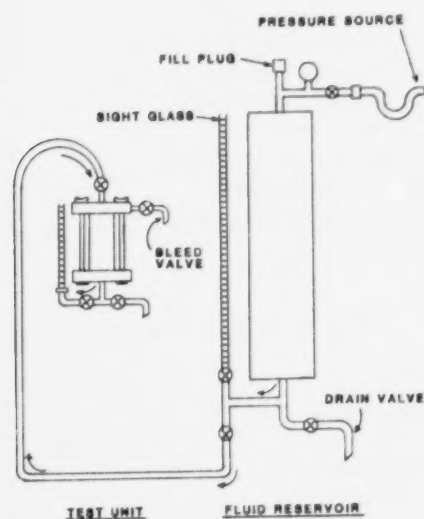
Method of Test

A standard method of test for evaluating the inhibiting effects of soil additives to migration of organics through soils was not available. Therefore, modification of standard permeability testing of soils was required for this work.

A constant head permeability method of test was utilized throughout the laboratory investigation. However, instead of using the standard up-flow of fluid through the core to be tested, a downward flow was used in all cases. A flow

diagram of the test apparatus is presented on Figure 1.

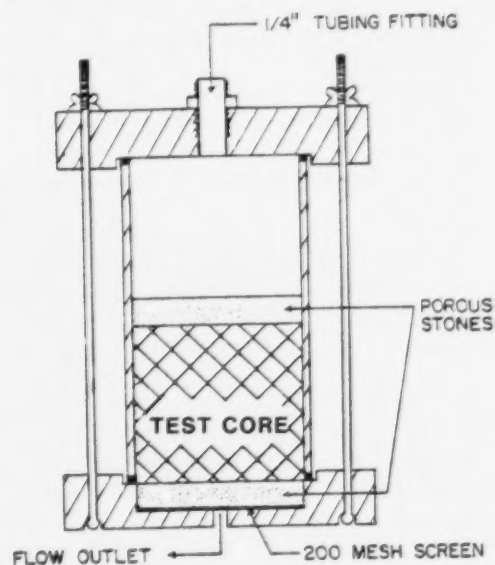
Figure 1. Permeability Test Unit



The test apparatus was constructed from major component parts purchased from Soil Test, Inc. This included one high pressure K-670 Miniature Permeater Unit plus two additional K-620 Soil Test Permeater Units. These were connected to enable three simultaneous permeability tests. Subsequently, a second test unit consisting of two permeaters and pressure reservoir was added to expedite the test work with contaminated water as a fluid.

Operating pressures from 6 psi to 20 psi were used to accelerate the tests. Constant pressures were maintained through the use of an air compressor attached to the fluid reservoir. The volume of fluid flows measured in a buret attached to each test unit (Figure 2), or by flowing into a graduated cylinder through the bottom drain valve.

Figure 2. Test Permeater



Pretreatment of the soils with the additives to be tested was accomplished by direct addition on a weight percent basis. Approximately 100g of soil mixture was prepared for each test. Following the addition of the additives, water was added as required during mixing to achieve a medium to stiff consistency prior to compression in the test mold.

The unconsolidated soils were prepared for testing using parts from a Harvard Miniature Compaction Apparatus. The tare weight of the mold or sleeve from the permeater plus a 200 mesh screen and a 3.0 cm porous stone was obtained. After clamping the mold in the mold holder, the screen was placed in the bottom of the mold. Approximately 30 cc of the soil to be tested was added and gently tapped or pressed into the mold. This amount of sample occupied approximately one-half of the total capacity of the mold. Water was added to maintain a saturated test core during compression. The porous stone was then placed on top of the

test sample in the mold and pressure applied with the collar remover press. This unit is equipped with a spring loaded plunger with a base plate approximately 3.0 cm in diameter. The pressure was applied by pushing down on the compression rod. In total, approximately 50 pounds per square inch was applied for a period of 60 seconds. After compressing the sample into the mold, the mold was removed and the final weight of the unit with the sample recorded. Prior to assembling the mold in the permeater the height and diameter of the test sample was measured and recorded.

Following assembly of the test units, water was added to the fluid reservoir. The reservoir was raised to the desired test pressure through the use of an air compressor. Prior to beginning the tests, sufficient water was added to each permeater to displace the air trapped above the test core through the upper bleeder valve. Once the test unit was filled with water, the tests were begun by measuring the flow through the core at various intervals of time.

The organic permeability tests were also prepared as described above. Following measurement of the water permeability, the inlet line at the top of each unit was disconnected and excess water above the test cores removed (approximately 25 ml). Approximately 25 ml of chlorinated hydrocarbon waste was then added through the inlet opening at the top of each test unit. The water line was then reconnected and the test resumed by measuring the flow of water or organics at various time intervals. Following passage of the organic wastes through the test core, the tests were continued to measure the permeability of water through the test core after exposure or contact with the organic waste.

Soils Tested

Various soils were tested for water and/or organic permeability during the course of the study. Some of these soils were samples taken from specific stratas encountered during the core borings. Some were composite mixtures of soil representative of the overall stratas that would be encountered in an excavation in the area. These included soils free from organic contamination and those which are currently contaminated in the proposed slurry trench area.

Several samples of different types of uncontaminated soil stratas found in the area down to a depth of 55 to 60 feet were evaluated for water permeability characteristics. The data were used to confirm the accuracy of the special test method used throughout the study and to develop background data for hydraulic flow in this area.

In addition to the above, a composite mixture of uncontaminated soils was prepared in proportion to the soils that would be encountered in the proposed slurry trench area. According to core borings the percentage of various types of soils down to a depth of 64 feet are presented on Table 3.

TABLE 3. COMPOSITION OF SOIL MIXTURE A (UNCONTAMINATED SOIL)

Soil Description & Depth	Percentage
Fine to medium tan silty clayey sand (0-16)	25.0%
Firm light gray and brown silty clay (16-19)	3.7%
Soft to very soft black organic clay (19-23)	6.2%

TABLE 3 CONTINUED

Light gray fine to medium sand (23-59)	56.5%
Stiff light gray and tan clay (59-63)	5.5%

A mixture of these types of soils was prepared from samples taken previously from the core borings. This composite sample, referred to as "Soil Mixture A" during the study, was tested for water permeability both with and without the addition of bentonite sealants.

A contaminated soil mixture, referred throughout the study as "Soil Mixture B", was also prepared from samples taken from the core borings in the area of the proposed slurry trench. This mixture was prepared by taking equal portions from samples taken every two feet during the drilling operations. The composition of soil mixture B is shown on Table 4.

TABLE 4. COMPOSITION OF SOIL MIXTURE B (CONTAMINATED SOIL)

Soil Description & Depth	Percentage
Tan silty clayey sand 0-12	20.8%
Tan and dark gray sandy (12-16)	6.9%
Dark gray to black silty organic clay (16-20)	6.9%
Silty, sandy clay (20-24)	6.9%
Tan fine to medium sand (24-60)	55.2%
Stiff gray and tan clay (60-62)	3.4%

Fluids Tested

Four different fluids were utilized during the investigation.

These included uncontaminated ground water, contaminated ground water, ground water which was saturated with chlorinated hydrocarbon wastes in the laboratory, and concentrated chlori-nated hydrocarbon wastes.

Two five gallon containers of contaminated water from the area were contained for testing. An analysis of this water was previously presented in Table 2. This water sample was used throughout most of the test work and is referred to as water in the balance of the report. The water is of a quality that could be expected to flow through the proposed slurry trench.

The concentrated chlorinated hydrocarbon wastes used throughout the investigation was a sample of API separator organic waste from the plant. Although the exact composition of this material was not determined, it is believed that this is similar in composition to the waste materials processed in earthen ponds in the past that was the source of the plume of contamination in the area.

Additive Materials Tested

Several oil additive materials were evaluated during the course of the investigation. These included two bentonite materials and cement flue dust. Although other possible additive materials are available, the scope of the project was limited to the first material found to provide a successful barrier to the flow of the organic waste.

The bentonite materials used in the investigation were Volclay Bentonite 125 (BENT125) and Volclay Saline Seal 100 (SS100). These materials are manufactured by the American Colloid Company, Skokie, Illinois 60077. Bentonite 125 is specially formulated for use in

slurry trench construction to reduce the flow of water. Saline Seal 100 is specifically formulated for use where the fluid to be controlled contains relatively high concentrations of salts and/or other contaminants.

The cement flue dust utilized throughout the investigation is a by-product manufactured by several cement plants located in Houston and Dallas, Texas. The sample of the cement flue dust tested was manufactured by Gulf Coast Cement in Houston.

PROBLEMS ENCOUNTERED

The only problems encountered during this series of tests involved the method of testing. Since no standard method was available for testing the permeability of organic constituents to slurry walls a modification of ASTM D-2434-68 was incorporated.

The first problem involved the density differences between water and chlorinated hydrocarbon waste. The ASTM method calls for flow from the bottom to the top of the sample cell. However, the density of the chlorinated hydrocarbon caused water, the displacement fluid, to pass by the waste material and directly through the soil. To alleviate this problem flow was introduced from the top of the cell to the bottom.

The chlorinated hydrocarbon was introduced directly into the sample cell before water was added from the top, as a driving fluid. This reduced the possibility of phase separation and allowed a slug of contaminants to be injected into the soil mixture.

The other problem involved the consolidation of soil into a stable form. As fluid was passed through

the soil mixture, mobile particles traveled to the confining screen and plugged the face of the sample cell, restricting flow. Porous stones were used as supplements to the screen to reduce the amount of face plugging by distributing mobile particles over a broader area. This eliminated the flow restriction and allowed long term testing.

RESULTS

On-Site Soil Permeabilities

The water permeability of various uncontaminated soil strata found in the area was determined in the laboratory using the modified test method. These data are presented on Table 5. When compared with the field permeability data of similar type soils in the area, these data indicate the modified test method, used throughout the investigation, produces results that are comparable with standard methods of test for field permeability measurements.

TABLE 5 - WATER PERMEABILITY OF UNCONTAMINATED SOILS

Core Depth	Permeability, cm/sec
3 - 5 feet	5.0×10^{-5}
5 - 7 feet	2.3×10^{-4}
20 - 22 feet	9.0×10^{-5}
50 - 52 feet	2.0×10^{-3}
62 - 63 feet	1.2×10^{-8}
Soil Mixture A	3.7×10^{-7}
0 - 63 feet	1.9×10^{-7}

Several samples of contaminated soil from the borings were also tested for water permeability. These included strata of soils encountered at various depths plus a mixture of soils found at various depths in the area of the proposed slurry trench. The data from these tests are presented on Table 6.

TABLE 6. WATER PERMEABILITY OF CONTAMINATED SOILS

Core Depth	Permeability, cm/sec,
0 - 12 feet	5.0×10^{-5}
12 to 25 feet*	2.1×10^{-7}
25 to 60 feet	4.4×10^{-3}
62 to 65 feet	1.8×10^{-8}
Soil Mix B	2.4×10^{-6}
0-62 feet	1.9×10^{-6}

* Zone of highest concentration of contamination

The fill material (0-12 ft) above the contaminated area had a permeability of 5.0×10^{-5} cm/sec. A mixture of soil in the zone of highest contamination (12 to 25 ft) had a permeability of 2.1×10^{-7} cm/sec. Contaminated fine to medium sand (25 to 60 ft) had a permeability of 4.4×10^{-3} cm/sec, or approximately the same as the uncontaminated sand from the same strata. A mixture of contaminated and uncontaminated soils throughout a depth of 0 to 65 feet below the surface (Soil Mixture B) had permeabilities of 1.9×10^{-6} cm/sec and 2.4×10^{-6} cm/sec. The difference between the permeabilities of the contaminated soil mixture (Soil Mixture B) and the uncontaminated soil mixture (Soil Mixture A) of approximately one order of magnitude is probably a result of the contaminated soil mixture containing a higher percentage of sand (60% vs 56%) plus a lower percentage of dense clay (2.6% vs 5.5%).

Permeabilities to water and organic liquids were also determined on several samples of contaminated soils as shown on Table 7. The permeability of Soil Mixture B to organics was 2.4×10^{-5} cm/sec as compared with an average initial water permeability of 2.7×10^{-6} cm/sec. The contaminated zone mixture

had a permeability to organics of 3.1×10^{-5} cm/sec as compared with an average initial water permeability of 3.3×10^{-7} cm/sec. It is interesting to note that although the initial permeabilities to water of these two soil mixtures differ by a factor of approximately 10, the permeability to organics was approximately the same. An attempt was also made to determine the permeability to organics of the stiff clay found at a depth of 60 feet below the surface. Although the clay exhibited an initial permeability of 1.8×10^{-8} cm/sec to water and continued to flow water throughout the test, there was no visible flow of organic through the test core as experienced during the other soil tests.

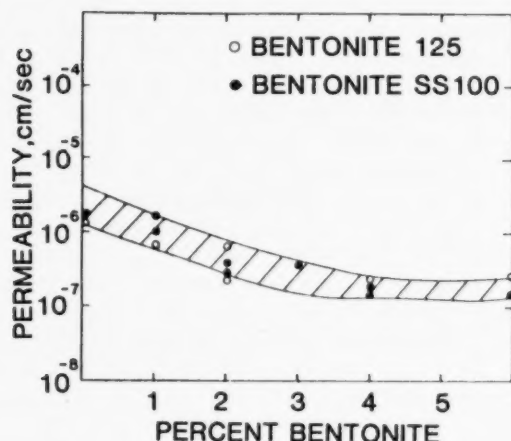
TABLE 7. PERMEABILITY OF CONTAMINATED SOILS

Soil Sample	W _I	O	W _F
Mixture B (0-62 feet)	10^{-6}	10^{-5}	10^{-7}
Contaminated (12-26 feet)	10^{-7}	10^{-5}	10^{-7}
Base Clay (60-62 feet)	10^{-8}	0	10^{-8}

Evaluation of Bentonite 125 and Saline Seal 100

A series of water permeability tests were conducted on samples of contaminated Soil Mixture B when treated with from 1% to 6% Bentonite 125 or Saline Seal 100. These tests were conducted to compare the performance of the two different bentonite materials in the presence of the contaminants contained in the on-site soil. The results from these tests are presented graphically on Figure 3.

Figure 3. Permeability to Water vs. Percent Bentonite



The data from these tests show the addition of of bentonite to Soil Mixture B results in a gradual decrease in the permeability of the soil to water. With 6% bentonite, the permeability was reduced from approximately 2×10^{-6} cm/sec to 3×10^{-7} cm/sec. Very little if any difference was observed in the performance of the Bentonite 125 and the Saline Seal 100 with the contaminated soil. However, Saline Seal 100 was selected for use in all subsequent test work due to its reported resistance to high concentrations of salts.

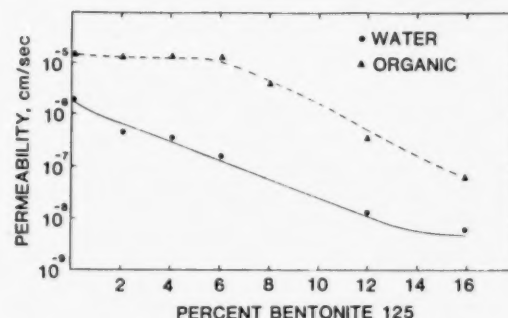
Permeability of Bentonite Treated Contaminated Soil

A series of tests were run to determine the water and organic permeability of the contaminated in-place soils (Soil Mixture B) when treated with up to 16% Bentonite 125 or Saline Seal 100.

When treated with increasing amounts of Bentonite 125, a proportional decrease in the permeability of Soil Mixture B to water and

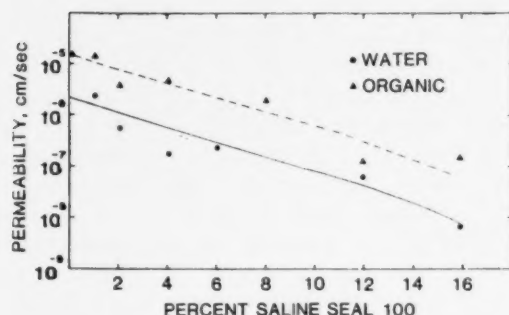
organics was observed. The average permeability to water was reduced from approximately 2.7×10^{-6} cm/sec down to 7.9×10^{-9} cm/sec with the addition of 16% Bentonite 125. The maximum permeability to organic was reduced from 2.4×10^{-5} cm/sec down to approximately 1.3×10^{-6} cm/sec at a 16% Bentonite 125 treatment level. In most instances, the permeability to water was shown to be approximately the same as it was immediately following passage of the organics through the test core. A plot of the permeabilities vs percent Bentonite 125 is presented in Figure 4.

Figure 4. Permeability vs. Percent Bentonite 125



Treatment with increasing amounts of Saline Seal 100 resulted in similar reductions in the permeabilities. To water, the average permeability was reduced from 2.7×10^{-6} cm/sec down to approximately 9.0×10^{-9} cm/sec with 16% SS100. The maximum permeability to organics was reduced from 2.4×10^{-5} cm/sec down to approximately 1.1×10^{-7} cm/sec at the 16% treatment level. A plot of the permeabilities vs percent SS100 is presented in Figure 5.

Figure 5. Permeability vs. Saline Seal 100



The data from these tests indicate treatment of a mixture of in-place soils in the area of the proposed slurry trench would require the addition of a minimum of 12% bentonite (Bentonite 125 or Saline Seal 100) to achieve a permeability of 1×10^{-7} cm/sec to water. Treatment with a minimum of 16% bentonite (Saline Seal 100) would be required to achieve a permeability of approximately 10^{-7} cm/sec or less to organics. Although limited data are available on a 16% Bentonite 125 treated soil, Saline Seal 100 appears to be slightly more efficient in reducing the permeability of the organic. At all treatment levels, however, the permeability to organics was shown to be 10 to 100 times greater than the permeability to water. A positive flow of concentrated organics through the test cores was observed in all of the tests regardless of the level of treatment.

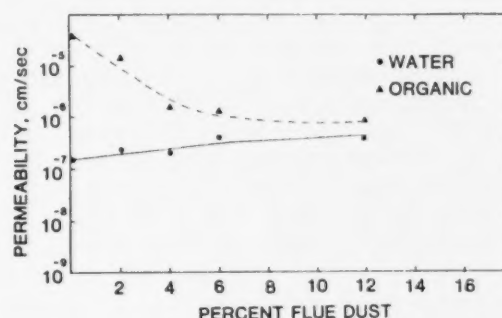
Cement Flue Dust/Bentonite Treated Soil

Several samples of Soil Mixture B treated with 6% and 12% Saline Seal 100 plus 1% up to a maximum of 18% cement flue dust were evaluated.

The addition of increasing amounts of cement flue dust to the 6%

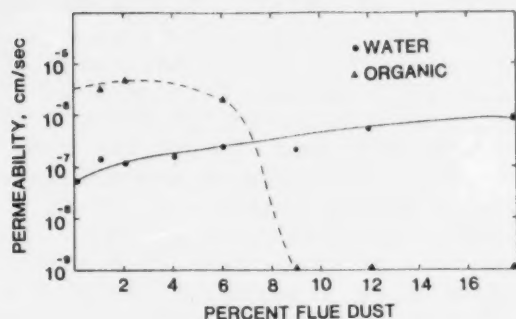
Saline Seal 100 treated soil resulted in a relatively small but corresponding increase in the permeability of the mixtures to water. The average water permeability increased from approximately 3.8×10^{-7} cm/sec with no flue dust up to 5.6×10^{-7} cm/sec with 12% flue dust. The addition of flue dust failed to reduce the permeability of the mixtures to organics. Permeabilities within the range of 1.7×10^{-6} cm/sec to 1.9×10^{-5} cm/sec were measured for organics. In all cases, the permeability to organic was shown to be higher than the permeability to water. Essentially all of the organic charged during each test was observed to pass through the test cores. The results from these test presented on Figure 6.

Figure 6. Permeability vs. Flue Dust (With 6% SS100 Treated Soil)



The addition of increasing amounts of cement flue dust to the 12% Saline Seal 100 treated soil resulted in a similar increase in the permeability to water. The average permeability to water increased from 1.7×10^{-8} cm/sec with no flue dust up to 9.5×10^{-7} cm/sec with 18% flue dust. The addition of cement flue dust to the 12% SS100 treated soil however had a significant effect on the permeability to organics at concentrations of 6% flue dust or greater. The results are presented on Figure 7.

Figure 7. Permeability vs. Percent Flue Dust (With 12% SS100 Treated Soil Mixture)



The addition 1% to 6% cement flue dust to the 12% Saline Seal 100 treated soil had little if any effect on the permeability to the organics. Essentially all of the organics charged to the units were observed to flow through the test cores. Permeabilities in the range of 1×10^{-7} cm/sec to 5×10^{-7} cm/sec were measured for water and 5×10^{-6} cm/sec for the organic.

Using concentrations greater than 6% flue dust mixed with the 12% Saline Seal 100 treated soil, the addition of organics to the system ultimately resulted in a sharp decrease in permeability with ultimate plugging of the core. Similar results were obtained with 12% and 18% flue dust. In most cases a small quantity of water (1 to 3 ml) was observed to pass through the core following addition of the organic. This was followed by a sharp decrease in permeability to less than 1×10^{-9} cm/sec with ultimate plugging of the test core.

Confirmation Tests

Several tests were conducted in the laboratory to confirm the initial positive test results on the 12% SS100/12% flue dust treated soils. Tests were also run to investigate

the effects of various other factors on the efficiency and long term stability of these systems. In addition, a test was run to confirm the initial results obtained on the stiff clay that underlies the area.

Permeability of 12% SS100/12% Flue Dust Treated Soil

A sample of Soil Mixture B treated with 12% SS100 and 12% flue dust was prepared and tested in accordance with the standard procedures used throughout the investigation. The resulting mixture exhibited an average permeability of 6.1×10^{-7} cm/sec to water. Upon contact with the organic waste, a sharp decrease in permeability was observed that ultimately resulted in plugging (permeability less than 1×10^{-9} cm/sec) of the core following passage of approximately 2.5 ml of water.

12%/12% Mixture with Contaminated Water

A sample of Soil Mixture B treated with 12% flue dust and 12% Saline Seal 100 was prepared for testing using contaminated water for hydration of the mixture. This test core exhibited an average permeability to water of 8.1×10^{-7} cm/sec. Following addition of organics to the unit, the permeability increased to approximately 1.1×10^{-6} cm/sec for the next 5 ml of fluid to pass through the core. During this period, approximately 1.5 ml of the 25 ml of organic charged to the unit passed through the core. Subsequently, a sharp decrease in permeability occurred with ultimate plugging and no flow of fluid through the core.

12% Flue Dust/12% SS100 Time-Set Compaction

A sample of Soil Mixture B treated with 12% flue dust and 12% Saline Seal 100 was prepared for

testing. In this test, the mold was filled with contaminated water and allowed to cure over a period of 12 days prior to beginning the permeability testing. This core exhibited a permeability of 5.2×10^{-7} to water. Contact with the organics resulted in a sharp decrease in permeability with plugging of the core following passage of approximately 3 ml water. No flow of organic through the core was observed during the test.

Water Stripping of Available Alkalinity

Analysis of the effluent water from previous tests using cement flue dust indicated an increase in pH from 7.6 up to 12.0 could be expected due to leaching of the available alkalinity in the flue dust from the treated soil mixture. A test was therefore begun to evaluate the long-term effects of water stripping of the available alkalinity from the 12%/12% system on the efficiency of the system to retard or prevent the movement of phased organics.

A sample of Soil Mixture B treated with 12% flue dust and 12% SS100 was prepared in accordance with the standard procedure for testing. The pH of the feed water and the effluent was 6.9 and 12.0, respectively at the start of the test. A gradual decrease in the pH of the effluent occurred during the course of the test. After three months, 7,300 ml of water had passed through the core and the pH of the effluent had decreased to 7.0. At that time, 22 ml of organics were charged to the unit.

The permeability of the test core to water remained relatively constant at approximately 3×10^{-7} cm/sec during the first 2,000 ml of water to pass through the core. The pH of the effluent at this point had

decreased to approximately 9.8. A gradual increase in permeability to approximately 3×10^{-6} cm/sec occurred during passage of the next 5,300 ml of water. Following the addition of the organics, permeabilities within the range of 1.0×10^{-6} cm/sec to 6.0×10^{-6} cm/sec were measured for the next 30 ml of fluid to pass through the core. This flow consisted of approximately 20 ml of phased organics of 10 ml of water. Subsequently, the flow consisted of water free from phased organics at a permeability of 5×10^{-6} cm/sec for the balance of the test. The pH of the effluent water at the end of the test was 6.9.

Effects of Contaminated Water on the 12%/12% Mixture

A sample of Soil Mixture B treated with 12% flue dust and 12% Saline Seal 100 was prepared in accordance with the standard procedure for testing. Saturated contaminated water prepared in the laboratory were used to determine the permeability to water. Approximately 2,000 ml of contaminated water was passed through the test core prior to contact with the concentrated organic waste. During this period, the pH decreased from 11.9 to 8.3.

An average permeability of 3.0×10^{-7} cm/sec was measured for contaminated water. On contact with concentrated organic, a sharp decrease in permeability was observed following passage of an additional 2.5 ml of water down to approximately 1×10^{-9} cm/sec. No phases organic passed through the core during the test.

Base Clay Permeability

An undisturbed sample of the stiff gray base clay that is found throughout the area was prepared for long-term testing for water and

organic permeability. The test core exhibited an average permeability to water of 4.9×10^{-9} cm/sec. Following passage of 4.1 ml of water through the core, 25 ml of organic was added to the unit. During the next 80 days approximately 25 ml of additional water passed through the test core with no visible organics in the effluent. An initial increase in permeability to approximately 1×10^{-8} cm/sec was measured immediately after the organic was added, followed by a decrease to within the range of 5×10^{-10} cm/sec and 6×10^{-9} cm/sec during the balance of the test.

DISCUSSION

The permeability of concentrated or phased chlorinated hydrocarbon wastes through the type of soils found above the stiff base clay in the area was shown to be substantially greater than the permeability of water through the same soils. A mixture of soils in the zone of maximum contamination (12 to 25 feet below the surface) in the area of the proposed slurry trench exhibited a permeability of 3.3×10^{-7} cm/sec to water and 3.1×10^{-5} cm/sec to the concentrated organic waste. A mixture of soil found from the surface down to a depth of 62 feet had a permeability of 2.6×10^{-7} cm/sec to water and 2.4×10^{-5} cm/sec to organic.

The stiff gray and tan base clay that extends throughout the area which was encountered at a depth of approximately 50 to 60 feet below the surface in the area of the proposed slurry trench was shown to be an effective barrier to the downward migration of the waste. This stiff clay was shown to have a permeability in the range of 4.9×10^{-9} cm/sec and 1.8×10^{-8} cm/sec to water. The clay was impermeable to the flow of the

concentrated or phased chlorinated hydrocarbon.

Treatment of the in-place soils to produce an effective slurry trench barrier to the migration of the phased organic waste was shown to be feasible using one or two different compositions. In-place contaminated soils when treated with 16% Saline Seal 100 exhibited a permeability of approximately 9×10^{-9} cm/sec to water and 3×10^{-7} cm/sec to the concentrated organic. In-place soils treated with 12% cement flue dust and 12% Saline Seal 100 exhibited a permeability of approximately 4×10^{-7} cm/sec to water but was shown to be essentially impermeable to the concentrated organic waste. On contact with the organic, a sharp decrease in permeability occurred and ultimately after passage of approximately 1-2 ml of water, the test cores plugged with essentially no further flow of water or organics.

The 12% flue dust/12% Saline Seal 100 treated soil mixture was shown to have a limited effective life time to prohibit or restrict the flow of phased organics. Water flowing through the mixture permeability in the range of 3×10^{-7} cm/sec to 4×10^{-6} cm/sec) resulted in stripping of alkaline constituents from the system and subsequent failure to restrict the flow of phased organics. According to the test data available from the contaminated water flow test and the long term water stripping test failure should occur following passage of from 73 to 225 trench volumes of water through the barrier. Under normal conditions, the amount of time required for this volume of water to move through the slurry wall would range from approximately 1000 to 3000 years.

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ADVANCED SECURE LANDFILL DESIGN

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ABSTRACT

Geologic and hydrologic conditions play an important role in determining the suitability of a particular site for creating a landfill. Often-times, poor sub-surface conditions will prohibit use of certain areas forcing waste generators to transport their residuals great distances for proper handling. The advanced secure landfill presented in this paper allows siting in less than optimal geologic/hydrologic conditions without adversely impacting the environment. The advanced design relies for its basis on many of the design elements incorporated into many of the conventional secure landfills being operated in the nation today. It expands these conventional designs by introducing innovative concepts such as dual underdrains and an in-situ leachate treatment system to insure groundwaters cannot become contaminated. It provides an opportunity to establish a landfill operation in a less than optimal setting without adversely impacting environmental quality.

INTRODUCTION AND PURPOSE

Landfills have been used historically for disposing of a multitude of different types of chemical and industrial wastes. As the volume of waste production increased, many landfills became over-burdened. The appearance of many new and often highly toxic constituents in these wastes combined with landfill containment failures due to poor design and/or less than optimal site selection led to public outcry. This public outcry continues to grow as more and more locations that are seeping contaminants into our groundwaters are identified.

The advanced secure landfill design presented, is an attempt to stem this growing tide of public opposition to landfill disposal by providing a technologically-defen-

sible approach toward containing hazardous wastes. It is a carefully engineered design which provides various back-up systems to insure that possible escape of leachate will not contaminate groundwaters.

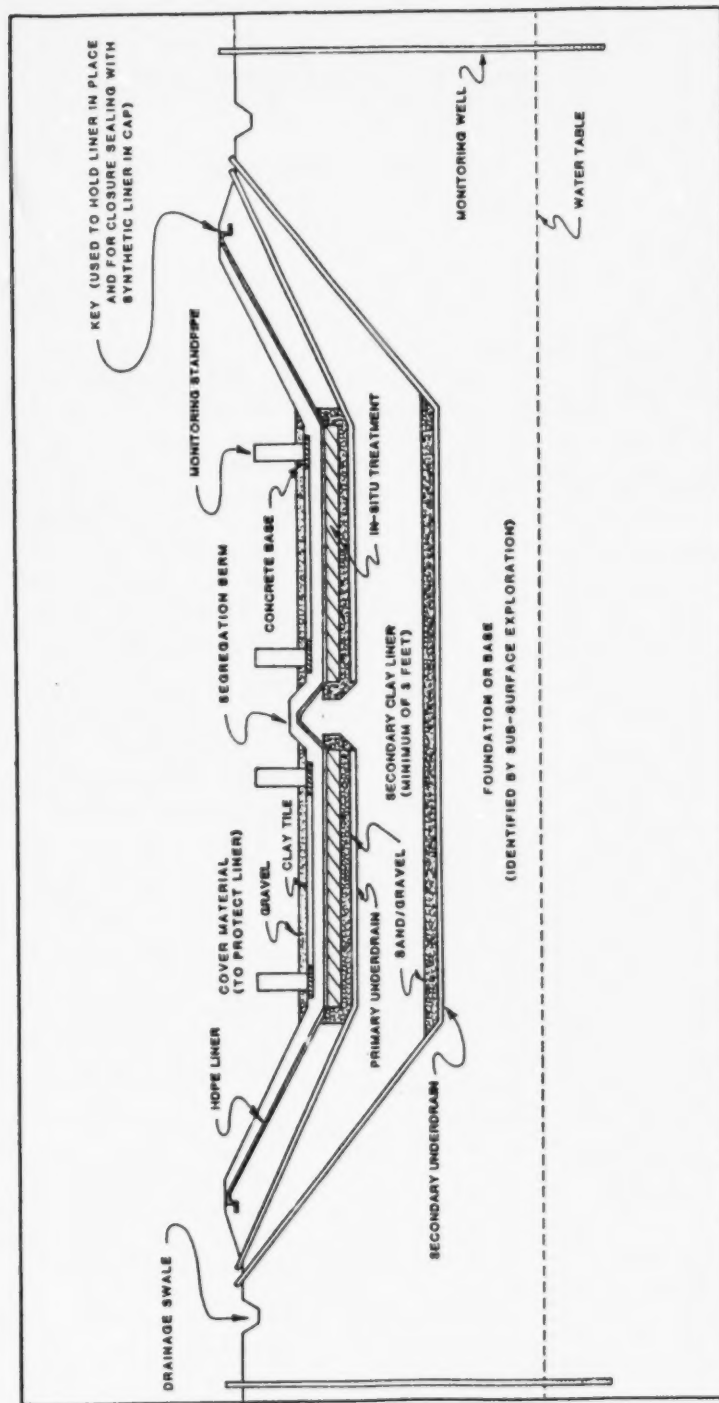
APPROACH

Conventional Design Elements

There are certain conventional design elements which have been developed and are currently utilized by some of the major regional HWMF's in the nation. These conventional design elements are the cornerstone and basis of the advanced design which was formulated.

Liners

The use of both natural and synthe-



ADVANCED SECURE LANDFILL DESIGN
(CROSS-SECTIONAL VIEW)

tic lining materials are incorporated into this design. The natural materials used are clay-type soils which given proper moisture content and compaction can be installed to provide a liner with a hydraulic conductivity of 1×10^{-7} cm/sec or less. In order to insure proper compaction it is recommended that clay liners be installed in 6" lifts.

There are a variety of synthetic lining materials placed over the entire interior surface of the landfill which can be used to augment the containment provided by a clay liner. Among the materials currently available are PVC (polyvinyl chloride), CPE (chlorinated polyethylene) and HDPE (high density polyethylene). The types of waste which are intended to be disposed of and the resistance of the lining material to the range of constituents in those wastes will dictate the best choice of synthetic liner.

In testing the various synthetic lining materials, a leachate of the treated (chemically-fixed) residues to be disposed of, would be used. The leachate would be an alkaline aqueous solution with trace levels of various organic contaminants.

The lining system as presented is a "laminate" which uses a compacted clay lining as a base beneath the synthetic liner. Overlying the synthetic liner is another clay lining which serves a two-fold purpose of providing a protective cover for the synthetic material in addition to supplying further containment.

Waste Segregation

The landfill cell design presented provides for waste segregation by establishing individual subcells or "compartments", within the landfill itself for various waste types. There are five subcells in the design:

- amphoteric
- heavy metal
- general
- halogenated
- toxic

The ability to separate these generic waste types from one another enables various cover materials to be utilized to immobilize many of the constituents in the waste. For instance, in the amphoteric subcell, waste carbonate tailings can be either admixed with the waste or used as intermediate cover material to create a buffered pH environment between 7 and 8 within the subcell. At these pH values, pseudo-metals such as arsenic and selenium and metals such as aluminum will tend to remain insoluble and less mobile. Application of alkaline cover materials such as hydrate lime tailings in the heavy metals subcell will create an alkaline pH environment tending to keep the heavy metals insoluble.

Separating the halogenated organic wastes from other organics in the general subcell enhances the long-term biodegradability of wastes in the general subcell, as does the segregation of toxic heavy metal containing wastes. Further, those halogenated residues where breakdown has begun to occur creating corrosive conditions can be neutralized with alkaline wastes to prevent the formation of acidic leachate.

Toxic Subcell

This subcell uses a double synthetic liner system. The "laminated", clay-synthetic liner-clay system, is overlain with a second synthetic liner of HDPE. This material has the greatest universal resistance to the halogenated and/or corrosive waste types anticipated to be handled in such a subcell. Once again the lining of HDPE is covered with a liner of compacted clay for protection and additional containment.

Internal Leachate Collection System

The upper clay lining installed in each subcell provides a relatively impervious base. Any rainfall which accumulates in the landfill and becomes leachate through contact with waste comes to rest on this base. The internal leachate collection system is the mechanism established to withdraw this leachate for processing before it is allowed to percolate significantly down through the initial clay lining. The system is composed of a tile underdrain, covered with crushed stone, that hydraulically connects two vertical monitoring standpipes. These vertical standpipes are 2'-3' diameter concrete sewer pipes with bell-ends placed one atop another as vertical filling of the landfill proceeds. The initial section of each standpipe is set in a concrete base and perforated around its circumference to allow for inflow of leachate. The perforated portion of each standpipe is covered with crushed stone which acts as a filter to prevent solids inflow and subsequent plugging of the standpipe. As leachate accumulates within a standpipe, it is removed by pump or vacuum truck for processing.

Innovative Design Elements

There are features of this advanced secure landfill design which are innovative and represent definite improvements over landfills constructed solely with the conventional design elements already discussed. Specifically, the use of a dual underdrain system and an in-situ leachate treatment system are innovative design features which make this advanced secure landfill superior to prior conventional designs.

Double Underdrain System

Although a single underdrain system has been in prior use in various conventional secure landfill designs, this is the first time a dual (primary and secondary) underdrain system has been proposed. The primary underdrain is located below the synthetic liner and actually serves as the base for the in-situ leachate treatment system. It serves as a device to both monitor the integrity of the synthetic liner and also remove treated leachate should a leak in the liner occur.

The secondary underdrain is located at the bottom of the excavation beneath the compacted clay liner which is below the synthetic liner. It allows the integrity of the clay liner to be monitored while also enabling any elevated water table levels to be withdrawn before infiltration into the clay lining and possibly into the landfill. Fluctuating and/or seasonally high water table elevations can be managed by using the secondary underdrain.

In-situ Leachate Treatment System

This is probably the most unique feature of the design since it has not been used to any extent in any other conventional designs.

It relies on straight forward chemical/physical principles associated with immobilizing the constituents in the waste types disposed of in the various subcells of the landfill. Beneath the synthetic liner in each subcell is a fixed bed of different porous media capable of sequestering or immobilizing contaminants associated with the leachate from that subcell. For instance, beneath the amphoteric subcell uniformly crushed limestone is placed while granular lime is used under the heavy metals subcell. The metallic cations which might be present in the leachate from the heavy metals subcell are precipitated by the alkaline conditions and enmeshed in the lime. The heavy metal-free aqueous liquid can then be withdrawn via the primary underdrain system.

Beneath the halogenated, general and toxic subcells, the fixed bed of porous media is comprised of granular activated carbon. A bed depth of 3" to 4" is sufficient to provide enough carbon to adsorb the soluble, high molecular organic contaminants in the leachate in these subcells. As long as this activated carbon is exposed to continually increasing concentrations of adsorbable organics in the leachate which it contacts (which should be the case during any post-closure liner failure/leachate leakage), it will function effectively. Once again treated aqueous liquid can be withdrawn using the primary underdrain system.

PROBLEMS ENCOUNTERED

In order to determine if the advanced secure landfill design is competitive with conventional designs, an economic analysis of the cost of construction of both a "shallow" and "deep" landfill for both the advanced and conventional designs was undertaken. The "shallow" landfill has a depth of 22.5 feet while the "deep" landfill has a depth of 47.5 feet. An additional variable, the location of the landfill with respect to the existing grade, was also considered in the comparative cost analysis. In the situation where 100% of the landfill is located above grade, the floor of the landfill cell is actually at ground level. In all cases the size of the landfill cell considered was 500' x 500' measured along the top of the perimeter berms. This gives a maximum disposal capacity of 147,200 cu.yds. for the shallow landfill and 260,000 cu.yds. for the deep.

Fixed Costs

There are certain cost elements in both the conventional and advanced designs which are independent of the depth below the grade we choose to locate the landfill. For the "shallow" and "deep" conventional and advanced landfills these elements are the synthetic liner and compacted clay to cover the liner:

Synthetic liner

"shallow"	275,000 sq.ft.
"deep"	325,000 sq.ft.

Primary clay liner

"shallow"	21,000 cu.yds.
"deep"	30,000 cu.yds.

Table 1: Construction Volumes ("Shallow" Landfill)
in thousand cubic yards

	% Above Grade		
	0%	50%	100%
	Con.	Con.	Con.
	Adv.	Adv.	Adv.
Excavation	150.0	75.0	-
Perimeter Berms	-	34.0	120.0
Cover Material	36.8	36.8	36.8
Primary Clay Liner	21.0	21.0	21.0
Secondary Clay Liner	-	-	-
Stockpile (Shortfall)	92.2	(16.8)	(177.8)
	182.2	116.2	(62.8)

Table 2: Construction Volumes ("Deep" Landfill)
in thousands of cubic yards

	% Above Grade		
	0%	50%	100%
	Con.	Con.	Con.
	Adv.	Adv.	Adv.
Excavation	295.0	108.0	-
Perimeter Berms	-	134.0	508.0
Cover Material	65.0	65.0	65.0
Primary Clay Liner	30.0	30.0	30.0
Secondary Clay Liner	-	-	-
Stockpile (Shortfall)	200.0	(121.0)	(603.0)
	245.0	271	(416.0)

Table 3: Cost Comparison ("Shallow" Landfill)
in thousands of dollars

	% Above Grade					
	0%		50%		100%	
	Con.	Adv.	Con.	Adv.	Con.	Adv.
Excavation	\$375.0	\$687.5	\$187.5	\$610.0	—	\$375.0
Perimeter Berms	—	—	\$85.0	\$85.0	\$900.00	\$195.0
Cover Material	—	—	\$4.0	—	\$184.0	\$184.0
Primary Clay	\$105.0	\$105.0	\$105.0	\$105.0	\$210.0	\$105.0
Synthetic Liner	\$165.0	\$165.0	\$165.0	\$165.0	\$165.0	\$165.0
Primary Under-drain	—	\$850.0	—	\$850.0	—	\$850.0
Secondary Clay	—	\$175.0	—	\$17.50	—	\$175.0
Secondary Under-drain	—	\$65.0	—	\$65.0	—	\$65.0
Total Cost:	\$645.0	\$2,047.5	\$626.5	\$2,055.0	\$1,459.0	\$2,114.0
Unit Cost: (per cu.yd.)	\$5.84	\$18.55	\$5.67	\$18.61	\$13.22	\$19.15

Table 4: Cost Comparison ("Deep" Landfill)
in thousands of dollars

	% Above Grade					
	0%		50%		100%	
	Con.	Adv.	Con.	Adv.	Con.	Adv.
Excavation	\$737.5	\$962.5	\$270.0	\$1,212.5	—	\$580.0
Perimeter Berms	—	—	\$612.5	\$335.0	\$3,810.0	\$2,632.5
Cover Material	—	—	\$325.0	—	\$325.0	\$325.0
Primary Clay	\$150.0	\$150.0	\$150.0	\$150.0	\$300.0	\$150.0
Synthetic Liner	\$195.0	\$195.0	\$195.0	\$195.0	\$195.0	\$195.0
Primary Under-drain	—	\$550.0	—	\$550.0	—	\$550.0
Secondary Clay	—	\$225.0	—	\$225.0	—	\$225.0
Secondary Under-drain	—	\$50.0	—	\$50.0	—	\$50.0
Total Cost:	\$1,082.5	\$2,132.5	\$1,552.5	\$2,717.5	\$4,630.0	\$4,707.5
Unit Cost: (per cu.yd.)	\$5.55	\$10.94	\$7.96	\$13.94	\$23.74	\$24.14

Variable Costs

There are various site-specific factors which will have a dramatic impact on the actual costs associated with the construction of a landfill facility using either the conventional or advanced secure landfill design.

There is a distinct possibility that regenerated activated carbon which is no longer suitable for conventional wastewater treatment applications can be used in the in-situ treatment system, drastically reducing the overall capital cost of the advanced secure landfill facility.

The tables which follow related the construction volumes and associated costs for the various scenarios considered.

It is understood that construction costs may vary widely between different geographic regions and many site-specific factors will influence actual construction costs. The cost comparison presented is not meant to establish an absolute capital cost estimate for constructing a facility since specific costs associated with site acquisition/ development, hydrogeological investigation, permitting, monitoring and ancillary equipment/structures were not included. The following unit costs were used to enable a valid comparison to be drawn between the two designs and to evaluate the impact the degree below grade would have on a proposed design.

Unit Costs

Excavation (assuming a uniform deposit at less than saturated conditions with a stable sub-base) \$2.50/cu.yd.

Perimeter Berms:
-obtain off-site soil and compact \$7.50/cu.yd.
-compact on-site soil \$2.50/cu.yd.

Compacted Clay
-obtain off-site clay and compact \$10.00/cu.yd.
-compaction on-site clay \$5.00/cu.yd.

Cover Material
-obtain off-site \$5.00/cu.yd.

Results

The comparative cost analysis bears out the fact for all cases with the exception of a "deep" landfill located entirely above grade, the conventional design is considerably less expensive than the advanced design. Although the conventional design presents a

less costly alternative in landfill construction, the costs associated with remedial action necessary to rectify groundwater contamination that might occur with this design can be several multiples of the total construction cost listed. The magnitude of these remedial action costs and the long term liability it represents to facility owners and to the government (if remedial action is required during or following the post closure period bears out the economic feasibility of the additional expense associated with the use of the advanced design.

Additionally economic feasibility for the advanced secure landfill design can be demonstrated if the distances from the source of waste generation to a permitted facility using a conventional design are considered. If one-way transportation charges of \$3.75 per mile for a bulk, 20 cu.yd. shipment of waste are assumed, the following table shows the "breakeven" distances in miles. If the distance between source of generation and a permitted landfill facility employing the conventional design are greater than those listed, the advanced secure landfill design can be justified on the basis of savings in transportation charges.

"Breakeven Point Transportation Distances (one-way miles)

	% Above Grade		
	0%	50%	100%
"Shallow"	68	69	32
"Deep"	29	32	--

Acknowledgements

The advanced secure landfill design presented is the property of Environmental Design, Inc. (Hwy.1, Jupiter, FL 33458) and is protected under U.S. Patent No. 4,430,021. Waste Resource Associates, Inc. acted as technical consultant to Environmental Design, Inc. in the development of the design and Randolph W. Rakoczynski is a co-inventor of the design along with Mr. Louis E. Wagner and Mr. Harold F. Flannery. Flannery & Esz, Inc. (Cincinnati, OH) have had considerable experience in the construction of secure landfill facilities.

Mr. Gary W. Catlin, Vice President of SLC Consultants/Constructors, Inc., an individual with considerable actual field experience in secure landfill construction, assisted in establishing the unit costs used in the cost comparison.

Currently, SolidTek Systems, Inc. is a licensee of Environmental Design, Inc. for the advanced secure landfill in the states of Georgia and Pennsylvania.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

DE-GASIFICATION OF EXISTING LANDFILLS

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ABSTRACT

De-gasification programs at waste landfills are undertaken for two purposes; resource recovery and landfill safety. This paper will describe a specific methodology to address safety problems posed by pressurized toxic gases at an uncontrolled waste disposal site. A conceptual design for a system to both investigate and relieve pressurized, and possibly toxic, gas problems is presented. The hypothetical case is for a landfill located in a populated area in which "zero release" of gases is a project constraint.

INTRODUCTION AND PURPOSE

This paper deals with a subset of sites that for one reason or another have (a) a combination of chemical constituents capable of producing toxic and/or volatile gases such as hydrogen sulfide, methane, chlorine, etc.; and (b) a geometrical configuration that would allow for the build up of pressure. Buried drums are the first such configuration that might come to mind. Other typical geometries are illustrated in Figures 1 and 2 where a "hard" crust forms a buried cap over a zone of waste materials capable of producing a gas. The crust, being relatively impermeable and of relatively high shear strength, allows for the build up of gas pressure. The gases may build up in pockets or in a relatively uniform zone, depending on the homogeneity and thickness of the crust, and the nature and quantity of the gas-producing waste material.

Upon penetration of a buried drum or a crust by a conventional geotechnical drilling rig, or by the unwary construction equipment operator during cleanup of the waste, the gas can be released in an uncontrolled manner, thus endangering the drillers, construction equipment operators, and possibly the public as well. Of course, if the concentrations are high enough and the pressure and/or quantity is high enough, the problem could have relatively serious implications.

In the oil and gas industry, the handling of unknown quantities of natural gas and occasionally hydrogen sulfide are practical problems encountered in the normal course of business and operations. These gas "kicks" are handled routinely, and in the case of hydrogen sulfide, there are established safety protocols for dealing with the

toxic nature of the gas. This industry has built up a wealth of experience, equipment, monitoring systems and safety procedures. It is the purpose of this paper to illustrate how the experience and background of the oil and gas industry can be used in conjunction with conventional geotechnical investigation techniques to investigate, relieve, or vent toxic gases from a shallow landfill in a safe controlled manner--either on an emergency basis or as part of a remedial action program.

APPROACH

The installation of toxic gas venting wells at a site such as shown in Figures 1 and/or 2, requires a combination of highly specialized skills that are not easily combined. For example, the depth is rather shallow, generally less than 50 feet; this is quite suitable for a typical geotechnical drilling rig. However, the presence of a toxic or volatile gas such as chlorine, hydrogen sulfide or methane at unknown pressure and concentration, requires the use of oil field techniques including extra heavy mud, possibly a blowout preventer (BOP), some type of mud-gas separator, shaker, and a degasser such as shown in Figure 3. The degasser removes the gas from the drilling mud and allows for transmission to a treatment unit such as a scrubber, or in limited cases to a flaring system. The extra heavy mud and possible BOP are both

required to assure a margin of safety consistent with the margins used in other parts of an EPA-sponsored cleanup. The heavy mud and the BOP require an oil-field type rig because of the need to use larger diameter drill pipe and casing, and heavy duty mud pumps. BOP's are not always readily available for small diameter drill pipe; and furthermore, the use of extra heavy mud (possibly 20 pounds per gallon) requires larger diameter drill pipe and adequate pump capacity. These are key factors in the technique which may preclude the use of a conventional geotechnical drilling rig.

The handling of the toxic gas requires a closed-mud system, also common to an oil-field driller but not to the geotechnical driller. As mentioned above, the system might include a shaker, possibly a mud/gas separator, and a degasser to allow for removal of the gas and transmission to some sort of treatment unit such as a scrubber. Mud tanks are used for mixing and handling the mud as opposed to mud pits. Here is an example where the experience of the geotechnical driller comes into play. The oil and gas driller is used to handling large quantities of mud, and consequently, the use of mud pits is the common practice. Shallow drilling for waste sites requires relatively small quantities of mud; and, therefore, mud tanks--the type that a geotechnical driller might use in a confined environment are more appropriate.

It is also noted in Figure 3 that we show an emergency "kill" line similar to that used for oil and gas drilling. This line allows for the addition of drilling mud under higher pressure should a fire or an unusual gas "kick" occur during drilling or development of the well. We also show the mud pump as being separated from the drill rig; however, the mud pump may very well be part of the drill rig in many applications.

TYPICAL INSTALLATION SEQUENCE

Generally speaking, the operation begins with the mobilization of a crew and equipment to the site. The field crew normally would have a project safety review before leaving the yard, including physical examinations and a review of the safety equipment contemplated for use at the site. The crew normally consists of five experienced members (superintendent, tool pusher/driller, driller/helper, power swivel operator, and well-site health and safety officer). We mention a power swivel operator as being a member of the crew because an oil well service rig equipped with a power swivel as opposed to a rotary mud rig is often the preferred type of equipment for this application. The crew is usually programmed to work an extended single shift as work during daylight hours is preferred; however, in many applications, round-the-clock operations are necessary. This is the norm in the oil and gas industry and does not present unusual operating problems.

Along with the service rig and power swivel, a mud-mixing system including a shaker and degasser are mobilized to the site. Material such as casing, drilling mud, cement, and so forth are ordered in quantities sufficient to complete a group of wells with the mud coming from a supplier retained to specify the mud program including mud-testing procedures. Cementing is generally delegated to a specialty oil field cementing service company as this requires special equipment not normally operated by the drilling crew.

The detailed technique for the venting well installation will vary from site to site, depending on particular conditions. The following steps would apply to a site having a geometry as shown in Figures 1 and 2 where the crust might be about 20 feet down from the surface and about two feet thick:

1. Construct an earth-drilling pad to support the drilling rig. Generally speaking, the surface will be relatively soft, too soft to support the drilling rig; and therefore, a drilling pad will have to be constructed with earth-moving equipment. In Figure 4 we show the use of geotextile material between the surface of the landfill and the earth-drilling pad.
2. Rotary drill an open hole with heavy mud to a point within about 4 feet of the

crust. Install steel surface casing and cement (the first stage) to surface using a specialty cementing service subcontractor. Casing is sized to permit the circulation of extra heavy mud, which is critical in subsequent steps in maintaining a closed system to mitigate random or unpredicted gas releases (Figure 4).

3. Connect the drilling tree (with blowout preventer, degasser and drill line connections) to casing and re-insert rotary drill tools (Figure 5).
4. Advance the hole using the rotary techniques through crust to a point about 4 feet below "crust." Use extra heavy mud and a mud program designed by the supplier. Circulate the mud through the shaker and degasser which is in turn connected to the scrubber (Figure 6). It is noted that during the drilling process the circulatory mud might bring waste liquids, such as organic solvents, from "old" drums to the surface.
5. If no gas kick occurs or after a kick is fully relieved, trip out the drilling tools and install production casing with closure valve through the surface casing. The bottom four feet of the production casing will be slotted or screened. Using a combination of external and internal

packers such as a formation packer collar and/or baffle plates set in at the crust, remove the mud above the packers and cement (second stage) the production casing to the surface (Figure 7).

6. Re-install a drilling tree over main closure valve. Trip in the small diameter drilling tools. Refill production casing with mud. Drill out the internal packer or knock out baffle plates.
7. Dilute the mud mix by washing through tools until mud is practically water. "Develop" the well to extent practical.
8. Trip out the drilling tools through BOP and stripper. Close the main valve on the production casing. Remove the drilling tree and install production tree (Figure 8).

At this point, the well is available for venting of the gas and its subsequent treatment at a scrubber or treatment unit.

HEALTH AND SAFETY

The members of the drilling crew must be thoroughly knowledgeable of the personal protection procedures dictated by the oil and gas industry and hazardous waste emergency response health and safety programs. Normally this type of project will employ EPA "Level B" protection with some minor

modifications to suit field conditions. For the example shown in this paper where the toxic gas is generated in the waste beneath the crust, the Level B protection would be employed when the drill tools are re-inserted into the cemented surface casing. Level B is not necessary for work above the crust because any gas encountered above the crust would be relatively low pressure and would be counteracted by the heavy mud with adequate margin.

Monitoring systems are set up around the rig and around the site fence line. For a hydrogen sulfide venting project, we would employ a battery-operated monitoring system sensitive to one PPM. This would be operated during drilling operations after the surface casing is installed if we are reasonably sure that the gas content of the waste material above the crust is minimal. Alternately, one might utilize an organic monitor and/or an explosive meter, or other appropriate real-time monitoring equipment.

SUMMARY

Remedial action programs and emergency response programs occasionally dictate the need for the relief, handling and treatment of pressurized toxic or volatile gases in relatively shallow lagoons and/or landfills. This paper presents a technique which combines the knowledge and experience of the oil and gas industry with that of the conventional shallow geo-

technical driller. This procedure results in an effective and safe means of installing relief wells without undue risk to drillers and the general public. The key factors in the operation include the use of an extra heavy drilling mud, a closed mud system, and the possible use of a blowout preventer. The techniques used herein are not new, and in some cases, would be viewed as relatively conservative applications of equipment that are used for much more dangerous situations such as those encountered in oil and gas drilling. The application in such shallow deposits as encountered in lagoons and landfills, however, does require some modification because of the shallow nature of the deposits.

ABOUT THE AUTHORS

Dr. Paul C. Rizzo

Dr. Rizzo is founder and President of Paul C. Rizzo Associates, Inc., a consulting organization based in Pittsburgh that works internationally on the solution and cleanup of waste problems--both nuclear and chemical hazardous waste. Dr. Rizzo received his Doctorate from Carnegie Mellon University, has published numerous papers, and has served on a number of international panels and committees dealing with environmental issues.

Mr. Carl M. Rizzo

Mr. Rizzo is co-founder and President of R & R Petroleum, Inc., a Pittsburgh based independent oil and gas

producer working in the Appalachian Basin of the United States. Mr. Rizzo has designed, supervised, and operated oil and gas drilling programs and production systems for wells as deep as 5,000 feet--the normal depth in Appalachia. Mr. Rizzo holds a Masters degree from the University of Pittsburgh and has worked both onshore and offshore on shallow drilling projects.

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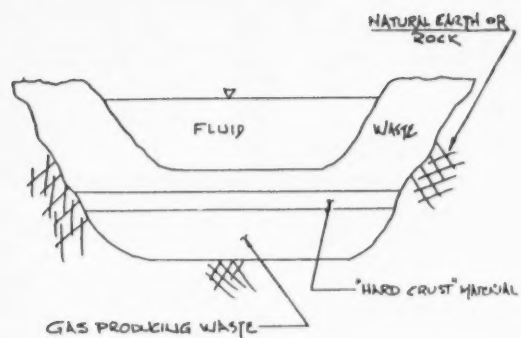


FIGURE 1

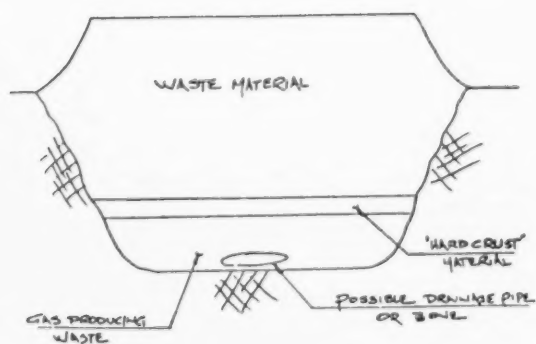


FIGURE 2

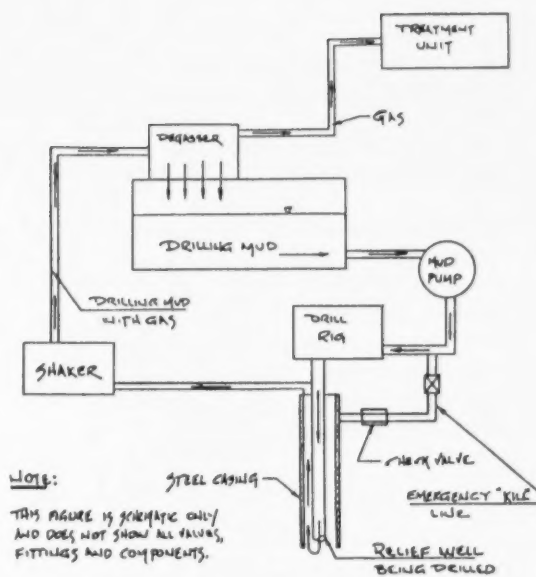


FIGURE 3

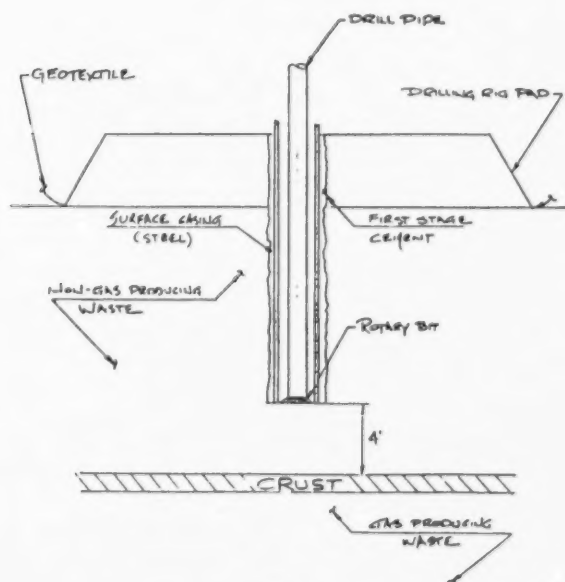
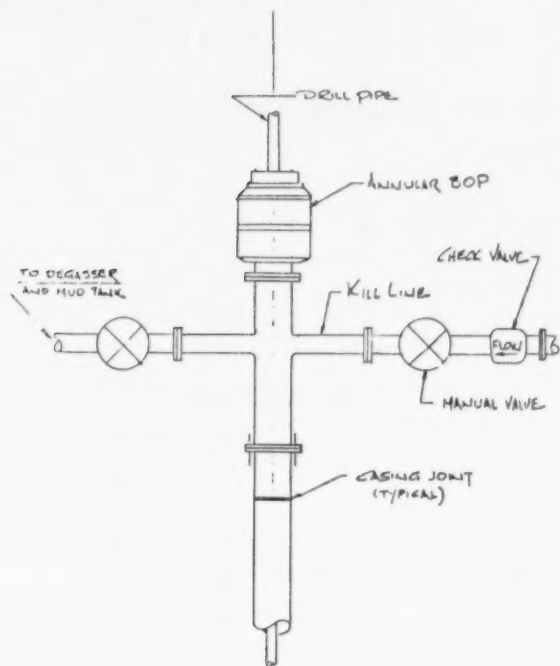


FIGURE 4



DRILLING TREE
FIGURE 5

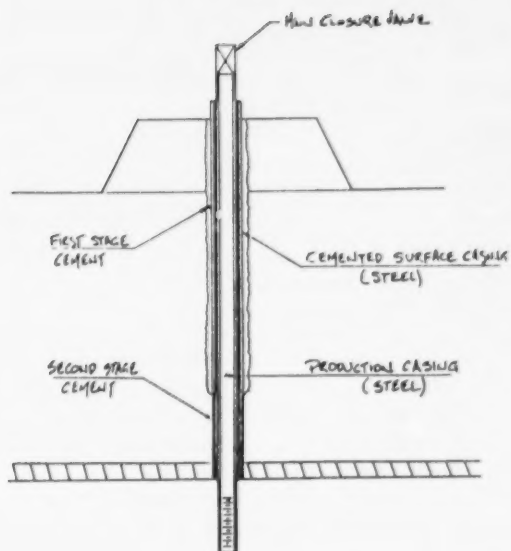


FIGURE 7

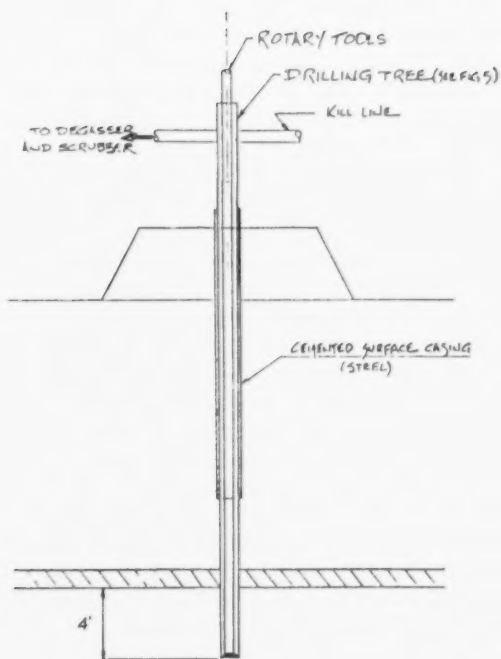
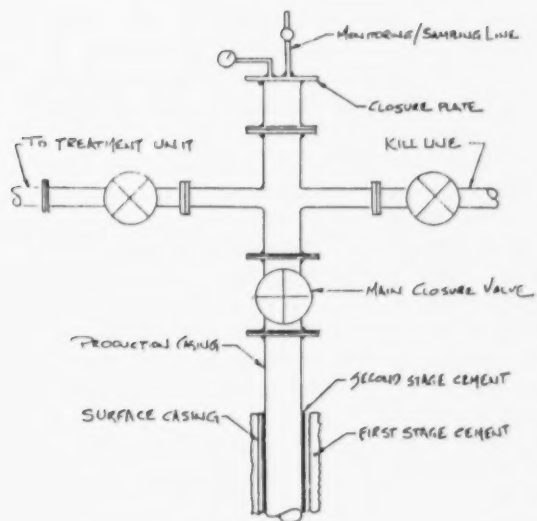


FIGURE 6



PRODUCTION TREE
FIGURE 8

FACTORS AFFECTING STABILIZATION/SOLIDIFICATION OF HAZARDOUS WASTE

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ABSTRACT

The stabilization/solidification of toxic wastes involves a series of chemical and/or physical treatment procedures. The waste is normally treated so as to complex or bind the toxic elements in a stable, insoluble form or to entrap the waste material in a crystalline matrix. A hazardous waste may contain many constituents that could interfere with the binding process. This recently initiated project is concerned with identifying possible interfering mechanisms between particular compounds and waste binding systems.

A synthetic sludge was produced containing parts per million concentrations of cadmium, chromium, mercury and nickel. The sludge is mixed with increasing concentrations of interfering compounds and then with selected waste binders. Various waste mixtures will be evaluated to determine the particular interfering effects on stabilization/ solidification processes. This paper provides an interim report on the progress of the study.

INTRODUCTION

The Environmental Protection Agency (EPA) is responsible for evaluating the suitability of hazardous waste for land disposal and for the examination of hazardous waste delisting petitions under the Resource Conservation and Recovery Act (RCRA) regulations. A thorough understanding of the potential behavior of stabilized/solidified waste is necessary to make judgements as to the effectiveness of contaminant containment. There are several methods available for the stabilization/solidification (S/S) of many hazardous wastes. The complexity of some wastes is such that some of the chemical components of the waste may interfere with the proposed S/S process and cause an undesired phenomenon (e.g. flash set, set retardation, spalling, etc.). There is a lack of quantitative data concerning the effects of these interfering components upon the particular S/S process. A study of the factors

affecting S/S of hazardous waste is designed to help fill that data void.

Background

Experience from the cement and asphalt industries, as well as radioactive waste solidification, has demonstrated that small amounts of some compounds can seriously reduce the strength and containment characteristics of binder/waste mixes used in S/S technologies. The common binding materials in waste S/S systems are derived from industrial cement and asphalt materials and some data are available on the effects of impurities on strength, durability, and permeability of structural cement mixtures. The cement industries have had to specify the types of cement, aggregate, and accelerators or retarders that will be permitted in portland concrete specifically because additives affect performance. Radioactive waste processors have had to develop limits for particular components that reduce the effectiveness of S/S of their wastes. In some

cases these interfering materials can produce set retardation so that hardening does not occur. In other cases, a waste constituent may cause a flash set or flash hardening so that effective mixing of the waste and binder cannot occur. Some waste constituents can react to cause swelling or disintegration of the solidified mass after setting. The effects of these interfering materials are often disproportionate to the amounts present in the waste.

Research that clarifies the relationship between the composition of the waste and performance of the binder can greatly help in evaluating the hazards of the materials. For example, minor organic components in a waste stream can significantly retard the cementing reaction, but these specific materials can be limited in a processor's treatment permit to assure that binding reactions occur, and that waste containment is not compromised. Similarly other deleterious compounds that cause flash sets or expansion reactions can be excluded where reactive binders are proposed.

When waste is placed for final disposal, there is always a possibility of the waste being unearthed by erosion or later excavation. The impact of stabilized/solidified material on its surroundings after exposure can be significant. The effect that interfering substances have on the durability of stabilized/solidified waste is a question of paramount importance.

PURPOSE

The purpose of this study is to develop technical background data on the compatibility of critical waste constituents with various waste binding agents (portland cement, portland cement with additives, lime-pozzolan cement, gypsum cement). Specific supporting objectives are as follows:

- (1) Perform physical tests and chemical leaching tests on waste/binder mixtures.

- (2) Investigate the relationship between the amount of interfering substance and the significance of the interference to waste S/S reactions.

- (3) Evaluate the durability of specific waste/binder mixtures to long-term outdoor weathering.

- (4) Participate in the joint Alberta Environmental Center/Environment Canada/USEPA/Industry project to investigate test methods for use in evaluating solid wastes.

This paper will report on the results and progress made as of May 1985.

APPROACH

The study is being conducted in two phases (Figure 1). The first phase (Phase I) was completed in December 1984 and included the following tasks:

- (1) Conduct a literature search and report on potential factors affecting solidification processing of hazardous industrial and radioactive wastes.

- (2) Selection of four waste/binder systems and ten potential interference materials.

- (3) Formulation and processing of stock synthetic waste to be used in preparation of test specimens.

- (4) Screening for various waste-to-binder ratios.

Phase II of the study will be conducted over a 24-36 month period. Samples of the selected waste/binder system and interfering materials will be tested and evaluated by the U. S. Army Engineer Waterways Experiment

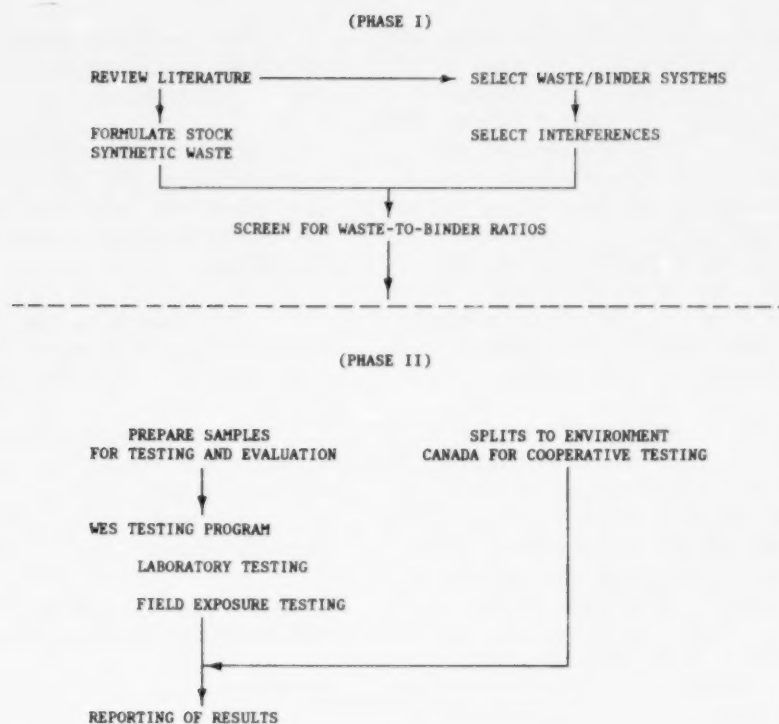


Figure 1. Simplified Study Approach.

Station (WES). Samples of stabilized/solidified waste will be tested for various physical properties and chemical leaching quality.

PROBLEMS ENCOUNTERED

The first experimental difficulty encountered in this study was the requirement to produce a synthetic waste sludge that was both reproducible and had stable physical and chemical characteristics. A hydroxide metal sludge filter cake has been formulated that meets this study requirement. The cake is prepared by taking a solution of metal salts, precipitating the metals with lime, and then vacuum filtering to produce a consistent filter cake of approximately 25 percent solid content.

RESULTS

Literature Survey

A review of the literature on solidification processing of waste showed that published information is limited which specifically relates to organic and inorganic interference phenomena in waste binding processes. Since most waste S/S systems incorporate various cement configurations, some inferences may be made between admixtures in cement chemistry and certain interferences in S/S processes.

Additives in Portland Cement Concrete

In the production of portland cement concrete, the use of chemical additives to control setting times, to reduce water requirements, to entrain air, and to create many other beneficial effects is common practice. The changes in properties

affected by additives are assumed to reflect fundamental changes in the hydration products, especially the crystalline calcium silicate hydrate. The chemical and physical development of concrete is complicated. The interfering effects of waste constituents on setting reactions compound the complicated nature of cement chemistry.

The influence of a limited number of organic compounds on the microstructure and engineering properties of hydrated cement has been investigated (Ramachandran, 1971). These compounds include sugars, lignosulfates, carboxylic acids, triethanolamine, and others. One inorganic substance, calcium chloride, an inexpensive and effective accelerator, has been extensively studied (Ramachandran, 1971). Calcium chloride accelerates hydration of tricalcium silicate. Morphological alteration of the hydrated calcium silicate gel and calcium hydroxide, along with changes in CaO/SiO_2 and $\text{H}_2\text{O}/\text{SiO}_2$ ratios, surface area, and pore-size distributions have been documented (Ramachandran, 1971; Odler, 1971; and Collepardi, 1972).

Interfering Mechanisms

In this section attention is given to conceptual models of interfering mechanisms. These models include interference via adsorption, complexation, precipitation, and nucleation.

Adsorption

One possible interfering mechanism is adsorption of additive molecules by crystalline particles thereby blocking the normal hydration reactions. Studies (Young, 1970) have shown that the retarding effect of organic compounds are related to their adsorption on metastable hexagonal calcium aluminate hydrates. The organic compound inhibits crystal

growth and conversion to calcium aluminate hydrates. The inhibiting effect roughly correlates with the number of hydroxyl, carboxylic, and carbonyl groups in the organic molecule. Hansen (1952 and 1959) noted the effect of two particular families of organic compounds, lignosulfonic acid derivatives and hydroxylated carboxylic acids, on setting reactions. Lignosulfonates are strongly adsorbed onto tricalcium aluminate (Blank, et al., 1963). The adsorption of calcium lignosulfonate onto tricalcium aluminate results in a relatively thick film or layer. The strong adsorption and thick layering of lignosulfonates onto tricalcium aluminate is indicative of a chemical reaction involving the organic and tricalcium aluminate hydration product. Taplin (1962) found retarding effects from aliphatic and aromatic dicarboxylic acids (e.g. maleic acid). In alkaline solutions where maleic acid has no hydroxyl group for a hydrogen adsorption bond, chelation may be the interference mechanism.

Although adsorption of organic retarders is primarily on tricalcium aluminate, retardation is due to adsorption on tricalcium silicate. There is no evidence of adsorption onto anhydrous surfaces. Organic additives can have an important bearing on reaction rates during cement hydration.

Complexation

Taplin (1962) related the retarding activity of organic compounds to the proximity of oxygen atoms to carbon atoms. He observed that the compounds with oxy-functional groups, in close proximity to each other, were also indicative of retarder effectiveness, and that chelation to metal ions could be an important factor in set retardation. Calcium ions can chelate with various hydroxyl or carboxylic acids, but the retarder or accelerators (respectively) are so

dilute that the complexation of the calcium is not an important factor (Young, 1972).

The effects of complexing calcium are more significant when the additive to affected-ion ratio is very large and when the affected ion is important to the setting system. Such would be the case for the aluminate and ferrite ions. Researchers (Kalousek, 1943, and Roberts, 1967) have shown that the addition of sucrose increases the concentration of alumina and calcium ions to above normal levels. Experiments (Young, 1972) with tricalcium aluminate indicate that 1 percent by weight additions of sucrose, succinic acid and tartaric acid increase the amounts of calcium and alumina in solution at first, but concentrations later decrease to normal or below normal. Silica concentrations are also increased when additives that affect alumina concentrations are used. Apparently, conditions in a cement paste are favorable to aluminate, ferrite and silicate ion complexation. It is possible that complexation delays the formation of hydration products. When cement forming ions are kept in solution by complexation, hydration barriers are established that retard the set. Waste components that chelate or complex toxic constituents may also accelerate their leaching even if the waste is successfully solidified.

Precipitation

The formation of insoluble precipitates by additives reacting with cement compounds is conceptually not a realistic mechanism of admixture interference. Certainly the formation of insoluble compounds could impede water transport, solubility, and subsequent hydration reactions. However, if retardation is due to precipitation, then the process should be non-selective. In this case, tricalcium silicate and

aluminate would both release calcium ions and the resulting effect on setting should be equally weighed among both compounds.

Nucleation

The inhibition of nucleation of crystalline calcium hydroxide by soluble silica is believed to be the self-retarding set feature of tricalcium silicate hydration. Growth of a crystalline matrix is retarded by the adsorbed silica ions when a hydrated calcium silicate gel layer results in a diffusion barrier to calcium hydroxide. Eventually crystal growth results in the adsorbed silica being trapped in the crystalline matrix as the hydration process continues. Prismatic growth of calcium hydroxide results from differential adsorption of silica on calcium hydroxide crystal faces (Young, 1972).

It is postulated that organic retarders act much the same as silica ions being adsorbed onto the calcium hydroxide nuclei. However because of more retarders being solubilized, the organic retarders are much more effective in being adsorbed and more completely cover crystal growth surfaces. The resulting retardation of crystal growth causes the formation of more crystallite nuclei in the saturated solution. The net effect of crystal growth on this many nuclei is acceleration of tricalcium silicate hydration following the initial retardation period (Young, 1972). A one percent (by weight) of a strong retarding agent, completely inhibits tricalcium silicate hydration. Addition of prehydrated tricalcium silicate has been found to overcome the effect of the organic retarder indicating the merit of an adsorption/nucleation model.

Effects of Organic Compounds on Physical Properties

Accelerators

Any compound that promotes the nucleation and growth of calcium hydroxide will be an effective accelerator. The most commonly used organic accelerator of hydraulic cement is triethanolamine (TEA). At addition rates less than 0.06 percent by weight of cement, TEA is an accelerator. At greater dosages, TEA is a retarder. Calcium formate is another common accelerator. The addition of calcium chloride to the cement mixture accelerates crystal growth by eliminating the necessity for ions to move from the Tricalcium silicate structure into solution. Both TEA and calcium formate have been shown to improve the 28 day compressive strength of Portland cement concrete. Formaldehyde and paraformaldehyde decrease the 28 day compressive strength at higher dosage rates (Roskopf, et al., 1975).

Retarders

Early strengths are lower in concrete specimens with retarders than those without. However, as the age of the specimens increase, those containing retarders generally have higher compressive strength and comparable flexural strength. The drying-shrinkages of specimens containing retarders are also comparable to those without retarders. It is interesting to note that soluble calcium salts which provide anions that adsorb onto the calcium hydroxide crystal surfaces cause a retarding effect (e.g. calcium nitrate).

Waste Binding Systems and Interferences Selected for Study

Portland cement, lime-pozzolan, and gypsum cement have been used in conjunction with other additives (e.g. flyash) to stabilize/solidify

industrial waste sludge. Lime-pozzolan mixtures are frequently used to convert liquids and semi-solids to a solid form. Systems selected for testing are those found in use in waste treatment and judged to have potential widespread application. Type I Portland cement and Type I Portland cement with flyash were chosen for immediate investigation. A lime-pozzolanic cement and a gypsum cement formulation will be used in subsequent experimentation.

Ten (10) materials with properties known or suspected to interfere with the S/S process were chosen for study. The frequency and concentration with which these materials are commonly found in waste streams considered for S/S processing were also considered. The interfering materials selected for study are: (1) oil and grease; (2) light weight oil; (3) phenol; (4) sulfates; (5) strong base; (6) pesticide; (7) degreaser; (8) lead; (9) copper; and (10) zinc.

Synthetic Waste Sludge Development

The synthetic sludge to be used in this study was generated by treating a synthetic wastewater containing cadmium, chromium, mercury, and nickel with hydrated lime to yield a hydroxide sludge containing these metals in concentrations at least 100 times that necessary to cause rejection on the basis of the EP Toxicity Test (eg. 100 ppm Cd, 500 ppm Cr and Ni, 20 ppm Hg). Synthetic wastewater was prepared in 500-gallon batches using the nitrate salts of the above metals. After allowing sufficient mixing time for equilibration, hydrated lime was added in a sufficient quantity to produce a pH of at least 10. Following a period of rapid mixing and slow mixing to allow for floc formation, the mixture was maintained under quiescent conditions for a minimum period of 24 hrs to provide for settling and sludge accumulation. Clear water above the

TABLE 1. REQUIRED SAMPLES FOR STABILIZATION/SOLIDIFICATION PROJECT-FY85

Processes: Portland cement and portland cement/flyash
Interfering Agents: Oil and Grease, oil, phenol, sulfate, caustic, pesticide, degreaser, lead, copper, and zinc

Test	Control (0 Percent)				2 Percent				5 Percent				8 Percent				Total Specimens	Required Samples
	Test Period				Test Period				Test Period				Test Period					
	24 hr	7 day	28 day	Specimens	24 hr	7 day	28 day	Specimens	24 hr	7 day	28 day	Specimens	24 hr	7 day	28 day	Specimens		
EP (dupl)			X	2			X	2			X	2			X	2	8	0*
Cone Index (dupl)	X	X	X	6 (2 x 3)	X	X	X	6	X	X	X	6	X	X	X	6	24	24
Unconfined compressive strength (trip)	X	X	X	9 (3 x 3)	X	X	X	9	X	X	X	9	X	X	X	9	36	36
Weight/density (dupl)			X	2			X	2			X	2			X	2	8	0*
Wet/Dry (15 cycles) (dupl except for control)			X	1			X	2			X	2			X	2	7	7 (4 in. diam)
X-ray and SEM (single except for control, test every third control)			X	0 or 1			X	1			X	1			X	1	3 or 4	0*
Permeability (single)			X	1			X	1			X	1			X	1	4	4 (2.8 in. diam)

* The weight/density measurement will be obtained using the 28-day Cone Index (CI) samples. After the CI is obtained, the samples will be broken into pieces and subsamples will be taken for the EP and X-ray/SEM tests.

sludge was decanted and the sludge transferred to a holding tank in preparation for dewatering. Dewatering to approximately 25% solids was achieved using a drum vacuum filter. Approximately 150 pounds of sludge is produced in each batch. Fresh sludge will be prepared on a regular basis so that all sludge used in the interference portion of the study will have a maximum age of seven days.

Work to be Conducted in FY 85

The initial laboratory work to be conducted in FY 85 will involve development of the required amounts for the S/S additives used in the portland cement and portland cement/flyash processes. These amounts will be established by preparing serial batches of solidified sludge, allowing representative samples to cure for 28 days, and determining the unconfined compressive strength (UCS) of each sample. A baseline dosage rate will be determined. The baseline dosage is the minimum dosage

required to produce a UCS of 100 psi using a minimum amount of additives. Work will also be conducted on the installation and calibration of equipment to be used later in the study, documentation of sample preparation and testing procedures, and the development and verification techniques for preparing and adding interfering agents to the synthetic waste sludge.

Work on preparation of solidified specimens of sludge containing the interfering agents is scheduled to begin in January 1985. Work will be conducted on one S/S process at a time. A list of the samples to be prepared and corresponding testing to be conducted is presented in Table 1. As indicated, aliquots of four sludge/interfering agent mixtures (0, 2, 5, and 8 percent interfering agent by weight) will be solidified and test samples prepared. All four aliquots will be obtained from the same batch of sludge. Testing will include EP, cone index, UCS,

weight/density, wet/dry durability, X-ray and scanning electron microscopy, and permeability. Cone index and UCS testing will be conducted on samples aged for 24 hrs, 7, and 28 days. Other testing will be conducted on 28-day samples. Sample preparation for each S/S process will require approximately 20 weeks. Data evaluation will be conducted on a continuing basis as test results become available.

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A PROCEDURE FOR CHARACTERIZING INTERACTIONS OF ORGANICS
WITH CEMENT: EFFECTS OF ORGANICS ON SOLIDIFICATION/STABILIZATION

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ABSTRACT

The effects of organics on the setting reactions of hydrating Portland cement and on the eventual structure of the hydrated cement paste have been studied by a combination of techniques including solvent extractions with solvents of varying polarities, scanning electron microscopy, energy dispersive X-ray analysis and X-ray powder diffraction. When ethylene glycol (EG) is solidified with cement, the EG appears to occupy at least 3 different kinds of sites, characterized by differing extractability. Gross alterations of the morphology of the cement matrix do not become apparent until rather large amounts of EG (EG/cement = 0.1 by weight) have been added to the hydrating cement mixture. At that point the structure is clearly weakened, and the EG is more readily extracted. However, at concentrations below the point at which major structural changes take place, there is evidence from X-ray diffraction that EG is entering the semi-crystalline calcium silicate hydrate (C-S-H) gel phase and altering its structure. Since the C-S-H gel phase comprises more than half of the hardened cement paste, alterations to that phase can be expected to alter the ability of the cement to immobilize wastes in solidification/stabilization processes.

INTRODUCTION

The present work was undertaken as part of a larger study of techniques of solidification/stabilization used for immobilization of wastes prior to landfilling, roadbed construction, etc. The technology has been most commonly studied as a potential technique for immobilization of toxic metal ions or radioactive waste.

Complete detoxification of metals by chemical, biological or other means is impossible short of elemental transmutation; hence, methods which dilute and/or isolate the metals are necessary as part of waste management schemes. Many vendors of solidification/stabilization technology have presented leaching data claiming to show the efficacy of various immobilization techniques; although claims con-

cerning the nature of chemical interactions between waste metal ions and the fixing agents have remained unsubstantiated(1).

The two principal constituents of most commercial fixing agents are cementitious materials (Portland cement, fly ash, etc.) and soluble silicates. A limitation often cited is that the processes are incompatible with organics, but details of such incompatibility are generally not available(2). A potential concern is that organics, even in small amounts, can alter the process sufficiently to substantially decrease the ability of the fixing agents to immobilize metal ions. Indeed, it is well known that organics can alter the setting characteristics of Portland cement. It is not clear whether, and at what concentration, organics interfere with the relatively complex setting reactions resulting in a significantly altered cement matrix. The question is of interest, not just with respect to solidification/stabilization technology, but also with regard to fundamental understanding of cementing reactions.

Polyhydroxy compounds are among the classes of organics which alter the setting characteristics of Portland cement. The effects of relatively small amounts (up to 0.5 percent) of triethanolamine (TEA) on the setting characteristics of Portland cement have been studied, mainly using differential thermal analysis, thermogravimetric analysis and conduction calorimetry(3). At amounts from 0.17 to 0.5 percent, TEA greatly accelerates the initial set, but retards the final set and produces a weaker cement structure. The results have suggested "a complex formed between

TEA and the hydrating components of portland cement."

The present study involves ethylene glycol (EG) and presents data relating to the presence of a chemical interaction between organics and Portland cement. Ethylene glycol was chosen for initial study for several reasons. It is completely miscible with water, and hence cement pastes can be prepared with any concentration of EG in water and in all cases a homogeneous liquid phase is being mixed with the unhydrated cement. Furthermore, there is evidence in the literature that EG does have profound effects on already set cement and the mineral constituents thereof(4,5). When hydrated cement or tricalcium silicate (C_3S) is treated with EG, etching occurs, but it is unclear whether mainly calcium silicate hydrate "gel" (C-S-H) or calcium hydroxide (CH) is dissolved(5).

APPROACH

The presence of a chemical interaction between water-soluble organics and Portland cement has been investigated by solidifying pure ethylene glycol (EG) with type I Portland cement and water. The cement used had the composition shown in Table I. Samples were prepared by weighing EG into a 20mL borosilicate glass, screw cap scintillation vial. Portland cement and water were added and the mixture stirred to apparent homogeneity with a glass stirring rod (ca. 1 minute of stirring). Samples were allowed to cure for variable lengths of time. Most of the samples in the present study were prepared using 4.0mL of water and 10.0g of cement and sufficient EG to give EG/cement weight ratios

Table 1 Percent Composition of Portland Cement Used in the Present Study

SiO ₂	20.6%
Al ₂ O ₃	5.2%
Fe ₂ O ₃	2.4%
CaO	64.9%
MgO	3.3%
K ₂ O	0.6%
SO ₃	2.9%

of 0.02, 0.04, 0.1, 0.2, 0.5 and 1.0.

Extractions of ground cement pastes were carried out with three solvents: dichloromethane (DCM) (dielectric constant = 8.9, polarity index(6) = 3.1); dimethyl sulfoxide (DMSO) (D = 47, PI = 7.2); and water (D = 80; PI = 10.2). After the appropriate curing time, the vials were broken and the samples were ground with a mortar and pestle to pass a 100 mesh screen. The powder and the pieces of broken glass from the vial were transferred to a 125mL Erlenmeyer flask, mixed with 120mL of solvent and shaken for 0.5 hour. The mixtures were filtered under suction using Whatman No. 41 filter paper and analyzed by gas chromatography using a Hewlett Packard HP5790A gas chromatograph coupled to a HP3390A integrator and a flame ionization detector. A 6 foot by 1/4 inch OD (2mm ID) 80/100 mesh TENAX glass column was used. Quantitation was performed using internal standards. For water and DCM extractions, 1,3-propanediol was the internal standard; for DMSO

extractions 2-propanol was the internal standard. In some preliminary work on solidification of decanol, gas chromatographic analysis was done using a 25 meter by 0.31mm ID 5% phenylmethylsilicone column and 1-octanol as the internal standard.

Examination of unextracted samples was also carried out by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). Each sample was cooled to liquid nitrogen temperature and then fractured into several small pieces, each approximately 1mm in diameter. A representative piece was mounted onto an aluminum stub for scanning electron microscopy in an ISI 60-A Scanning Electron Microscope (SEM). Prior to examination, the mounted sample was coated with a 20 nm film of Au-Pd in a Hummer VI Sputter Coater.

The SEM was operated at 15-30 keV accelerating voltage with the vacuum chamber at a pressure of less than 5×10^{-5} torr. When fine surface textures were observed at high magnifications, the lower voltages were necessary in order to reduce beam penetration. Microchemical analyses were made with an EDAX-ECON 2 Energy Dispersive X-Ray Analyzer and x-ray powder diffraction analysis by a GE X-Ray Diffractometer with a magnesium target.

PROBLEMS ENCOUNTERED

Sample Preparation and Reproducibility

At the outset of the project we anticipated using organics of a number of different types and in a wide range of concentrations. The result of this is that the "solidi-

fied" samples vary greatly in character from solid masses much like set cement, to non-solidified "soups", to solid mass with free-standing liquid.

None of the standard methods of specimen preparation is strictly applicable to the conditions associated with the present research. Due to the heterogeneous nature of some of the samples, reliable partitioning of large solidified samples would not be possible. Hence each sample needs to be prepared separately and must be capable of being transferred quantitatively at each stage from mixing to curing to analysis. An additional concern in our work has been to limit the volatilization of the organic admixture. These experimental restrictions have led us to choose to prepare and cure samples in the same container and to use sealable glass vials. In the sealed vial the partial pressures of water or organic vapors above the solid probably rapidly reach equilibrium values, although it is possible that as setting reactions continue, those equilibrium partial pressures may change slightly. Special temperature control is not being applied, and room temperature is in the range $23^{\circ}\pm 2^{\circ}\text{C}$. Samples are being stored in the dark to avoid any possibility of photochemical reactions of the organics.

We were concerned with reproducibility from the beginning because of the large number of samples being prepared. The best indicator we have that assures us of reliable sample replication is the extraction behavior. With occasional exceptions we can reproduce the amount of organic recovered from solidified samples prepared

by our standard procedure and cured for the same length of time so that the standard deviation is <10 percent of the average of the values in three to six replicates. Usually it is <5 percent. These results give us confidence that the trends we are seeing are real.

RESULTS

Some differences in the samples prepared with differing EG/cement ratios are obvious to the casual observer. At the weight ratios from 0.02 to 0.2 the mixtures harden, but the 0.5 and 1.0 ratio mixtures do not. Even at the 0.2 ratio, the surfaces of the solidified material appear moist.

The extractions with solvents of differing polarities give information regarding the extent and reversibility of binding of organics to the cement matrix. Changing solvent polarity would be expected to have a number of possible effects on the extraction behavior. Intermolecular interactions between EG and the solvents, particularly dipole-dipole and hydrogen bonding will increase in strength in the order $\text{DCM} < \text{DMSO} < \text{H}_2\text{O}$. The solvent interactions with the cement matrix will also vary. The ability of H_2O to dissolve $\text{Ca}(\text{OH})_2$, and perhaps other constituents as well, out of the cement paste may mean that water penetration into the material will be greater than that of the other solvents, thus having the effect of freeing more of any organic which was simply physically trapped in areas of the matrix inaccessible to the solvent. We are not convinced that the latter argument is valid under our conditions. When 1-decanol, a quite nonpolar organic, is solidified with cement and

extracted with DCM, >85 percent of the decanol is recovered. The matrix may be different in the presence of decanol than in the presence of EG, but our grinding and extracting procedure clearly does free most of the physically entrapped organic.

Some results of extractions of 1 month old samples are shown in Table 2 and are expressed as percent recoveries of EG. Our expectation that increasing solvent polarity would result in increasing recovery of EG was borne out. The results are clearly not due simply to solubility effects, since EG is very soluble in all three solvents.

Table 2 Percent Recovery of EG in Extractions with Various Solvents at Differing EG/Cement Weight Ratios

Wt. Ratio	DCM	DMSO	% Recovery	
			dil*	dil**
0.02	3.7	12	79	95
0.04	3.4	11	79	87
0.10	6.5	15	89	76
0.20	7.0	43	83	79
0.50	5.1	54	79	79
1.0	4.8	-	84	81

* The water solution was initially 0.05M in Na_2CO_3 and 0.05M in NaHCO_3 , with an initial pH of 9.9. The pH after extraction was 13.

**The water solution was initially 0.05M in acetic acid and 0.1M in sodium acetate, with an initial pH of 5.0. The pH after extraction was 12.

Since DCM and DMSO extract relatively small amounts of EG (compared to water), and since our procedure appears to free most physically entrapped organic, the reasonable conclusion to draw is that there is some chemical interaction between EG and the cement matrix that is stronger than the EG-DCM or EG-DMSO intermolecular interactions. The interaction that is certainly present is hydrogen bonding, and that interaction alone is probably sufficient to explain the relative extracting abilities of the 3 solvents.

The loading of EG on cement might be expected to influence extractability very substantially, since bound EG could be in quite different environments, and the cement matrix might be quite different at different EG concentrations. Surprisingly, any effect is obvious only in the case of DMSO extraction. In that case there is a major break in behavior between weight ratios of 0.1 and 0.2. We have concentrated on that concentration range in the microstructural characterization to be described below.

The extent to which any EG is irreversibly bound in the cement matrix has been investigated by repeated extractions of the same sample with water and DMSO (Table 3). In these experiments the solid residue after the initial extraction was treated with a second 120mL of solvent, reshaken, refiltered and analyzed. The samples were only ground one time. All of the EG has not been recovered after 5 extractions with the most aggressive solvent, water. Evaporative losses are possible, but we are using very non-volatile organics; and deliberately allowing the

Table 3 Percent Recovery in Repeated Extractions of 0.04 EG/cement Samples

Extraction No.	% Recovery*	
	H ₂ O**	DMSO
1	88	12
2	5.2	1.8
3	0.53	0.4
4	0.16	-
5	0.13	-
TOTAL	94.2	14.2

* Expressed as percent of the original amount of EG in the sample.

** Deionized water.

solids to stand open to the air for an hour or more prior to extraction did not appear to affect the results. A similar phenomenon was observed in extractions of 0.1 weight ratio 1-decanol/cement with DCM. After 3 extractions 97 percent of the decanol was recovered, and decanol could not be detected in the fourth extraction. We conclude from the decanol results that there are sites in the matrix where physically trapped organic is isolated from contact with the extracting solvent. Water is a much more aggressive solvent than DCM and can be expected to etch the cement matrix, and yet even after 5 extractions there are significant amounts of EG unaccounted for. We conclude that there are sites where EG is bound more tightly than by surface hydrogen bonding and/or that there are sites in the cement

matrix that are very poorly accessible to water.

The age of the sample does affect extraction behavior (Table 4). Again the DMSO extraction seems most sensitive to changes in the environment of the EG. The hydration reactions will be only partially complete at 7 days of cure. The DMSO extraction results, in comparison to the H₂O extractions, suggest that there are at least two qualitatively different

Table 4 Percent Recovery of EG in Extractions with Various Solvents at Various Times of Cure

Wt. Ratio*	% Recovery	
	7-day Cure	28-day Cure
	<u>H₂O Extraction</u>	
0.04	79	79
0.1	74	78
	<u>DMSO Extraction</u>	
0.04	11	7.4
0.1	27	16
	<u>DCM Extraction</u>	
0.04	4.8	3.6
0.1	6.8	7.1

* The samples in this table were prepared in a different manner from those cited elsewhere in the paper. In all these samples, regardless of the EG/cement ratio, the ratio of volume of liquid to weight of cement was kept constant at 0.4.

environments in which EG finds itself, a more tightly bound one and a less tightly bound one; and the proportion of EG in the more tightly bound environment is higher at lower EG concentrations and at longer times of cure.

SEM Observations

A calcium silicate hydrate (C-S-H) gel phase constitutes approximately one-half to two-thirds of the volume of hydrated pastes, and consequently, strongly influences their behavior.

Calcium hydroxide crystals constitute 20-25 percent of the paste volume. As the paste ages, the calcium hydroxide becomes an increasingly prominent constituent of the microstructure. Researchers utilizing the electron microscope to characterize Ca(OH)_2 commonly observe hexagonal plates. The scanning electron micrographs reveal the presence of this phase in both plain and waste containing cements.

Of considerable practical interest is the concentration of organic required to make significant changes in the cement matrix. It is reasonable to assume that if the matrix is considerably altered, the ability of the matrix to immobilize both metal ions and organics will be altered. SEM observations of the gross morphology of fracture surfaces of the solidified samples reveal few obvious differences between specimens of hydrated cement alone and hydrated cement containing "low" concentrations of EG. At the 0.1 weight ratio, however, significant differences are obvious. Figure 1 shows micrographs taken at relatively low magnification under conditions as

nearly identical as possible. In the figure, a contains no EG, b: 0.04 EG/cement, c: 0.1 EG/cement, d: 0.2 EG/cement. At higher magnifications it is possible to find features that have similar appearances, particularly in a, b and c. However, the differences in appearance are strikingly evident in the general views at 300X. In particular, massive structures and regions of crystallinity become much less common as EG concentration increases, until finally d bears little resemblance to a. The differences between a and b might well go unnoticed if the other members of the series were not available for comparison.

X-Ray Powder Diffraction Observations

Each sample was analyzed by x-ray powder diffraction prior to each microstructural analysis. This has been found to be very useful since changes in the crystalline components of the waste/binder sample can be determined if the quantities of the phases are sufficient. Figure 2 shows XRD data in a graphical form for the same 4 samples shown in Figure 1, also identified here as a-d. The trend away from crystallinity as EG concentration increases is evident in these graphs, as it is in the micrographs. The trace for sample d is quite featureless compared to that for the other samples. It is worth noting that in the two samples at lower EG concentration, the same general features are apparent as in the cement control sample. The crystalline component of hydrated cement that is easiest to identify is Ca(OH)_2 . One of the prominent Ca(OH)_2 peaks is identified on the plots along with peaks ascribed to

C-S-H gel. Even sample b shows distinct changes in the fine structure of the peaks associated with C-S-H gel. It thus appears that while the crystalline, or semi-crystalline phases characteristic of hydrated Portland cement continue to be present as significant quantities of organic are added to the hydrating mixture, there are significant changes in the amorphous or semi-crystalline C-S-H gel phase at relatively low organic concentrations.

CONCLUSIONS

When EG is solidified with cement, the EG appears to occupy at least three different kinds of environments. At high concentrations of EG, there is a significant amount of very loosely bound EG, which can be extracted readily by either DMSO or H₂O. The second environment contains more tightly bound EG, probably bound to surfaces by hydrogen bonding, and such EG can be readily extracted by H₂O but not by DMSO. The EG still remaining after repeated extractions with H₂O or DMSO can be considered to occupy a third environment. Conceivably this environment could be one in which EG replaces water of crystallization in some of the crystalline structures. However, the alterations that are obvious by XRD are those in the semi-crystalline C-S-H gel phase, and we suggest that the EG is located there. The Feldman-Sereda model(7) of hardened cement paste includes an environment for water between layers of C-S-H. EG could substitute for water in such an environment and be both chemically bound, probably mainly by hydrogen bonding, and also physically inaccessible to extracting solvents.

The EG being added to solidifying cement does not have an effect on the developing cement matrix which is obvious to the naked eye until the concentration of EG is rather high (EG/cement = 0.2). At that point the changes in structure can be seen in the SEM, but are also obvious to the naked eye. At lower concentrations, however, there are more subtle changes, which are clearly evident to XRD. The changes appear to involve the semicrystalline C-S-H gel phase, which normally makes up more than half of the volume of hydrated cement structure. Changes in that phase will clearly influence the physical characteristics of the hardened material as well as its ability to immobilize metal ions.

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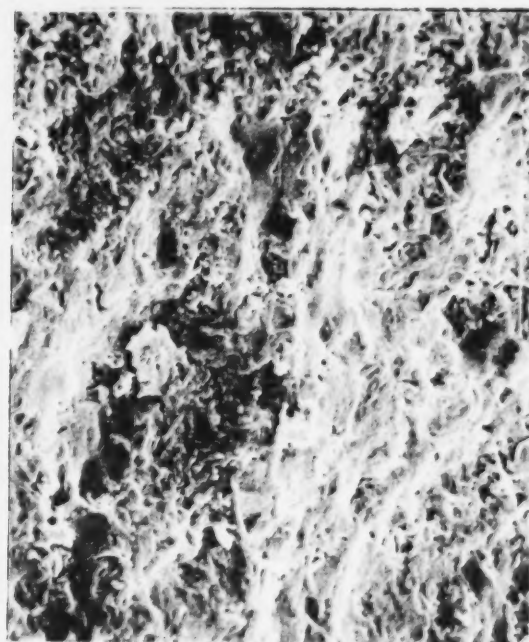
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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.



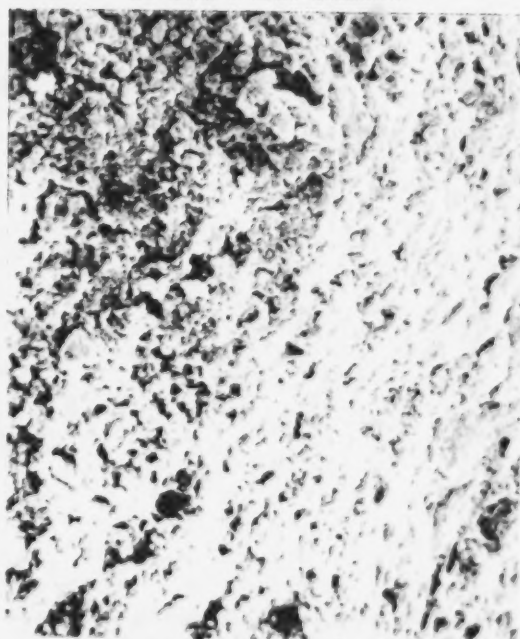
a. CONTROL



b. 0.04 EG/cement



c. 0.1 EG/cement



d. 0.2 EG/cement

FIGURE 1. MICROGRAPHS OF
VARIOUS ETHYLENE GLYCOL/CEMENT SAMPLES AT 300 X

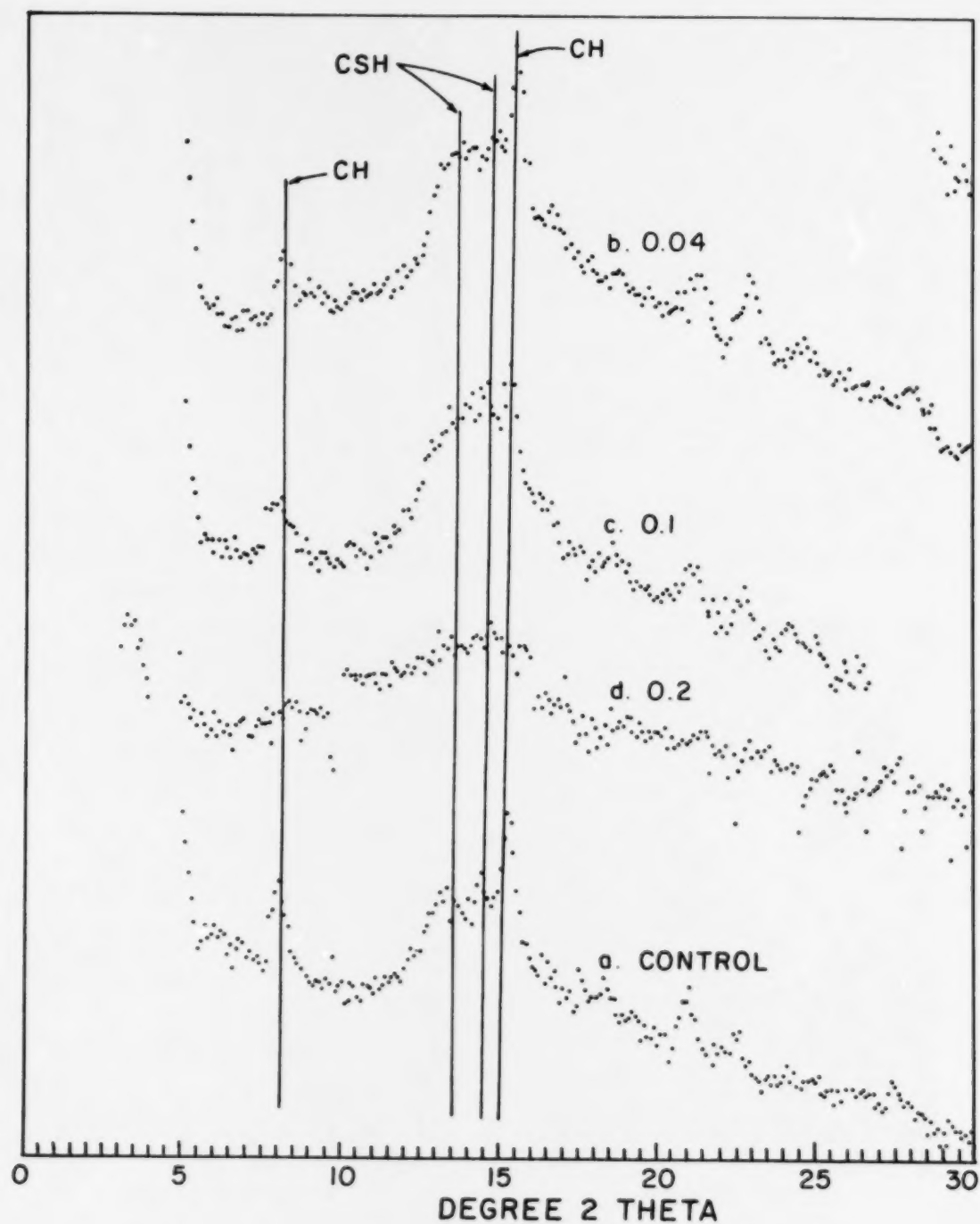


FIGURE 2. X-RAY POWDER DIFFRACTION OF VARIOUS ETHYLENE GLYCOL/CEMENT SAMPLES

THE RATIONAL USE OF CEMENT-BASED STABILIZATION
TECHNIQUES FOR THE DISPOSAL OF HAZARDOUS WASTES

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ABSTRACT

The mechanism of zinc and mercury fixation by a cement/sodium silicate stabilization process has been assessed from leaching, scanning electron microscopy, X-ray diffraction and porosimetry studies. The results of these tests correlate closely and suggest the operation of two separate fixation mechanisms. The presence of zinc has a significant effect upon the hydration and final physical properties of the final product. Mercury and related metals which do not form precipitates at elevated pH levels are held in pore solution. The importance of microstructure in metal fixation and also metal leaching from the cementitious matrix has also been demonstrated. The calcium aluminate hydrate structure, ettringite, has been identified as to be related to the structural integrity of the solidified product. The understanding of the mechanisms of action can enable a rational, cost effective approach to process design and operation to be achieved.

INTRODUCTION AND PURPOSE

A number of pretreatment processes have been developed to render industrial wastes suitable for final disposal. Waste stabilization methods based upon ordinary Portland cement (OPC) or other pozzolanic materials provide one form of pretreatment with landfill as an ultimate disposal route. The mobilization of wastes into water has always been a major consideration in containing toxic waste, and as such, much of the emphasis or stabilization processes has been placed on preventing the waste from coming into contact with water and controlling the chemical conditions of the aqueous environment in order to minimize solubility.

The mode of interaction of the inorganic waste and the stabilization system will clearly influence the leachability of the metal (1). Leaching studies of certain metals stabilized in a cement matrix have shown that the amount present in the leachate is often considerably lower than the calculated value based upon the theoretical solubility product. A variety of fixation mechanisms have been postulated to account for this, involving absorption by cement hydrates, substitution and solid solution in the hydrate structure, and formation of insoluble compounds. However, many of these claims are related to semi-quantitative observations and interpretations, leaving many of

the fundamentals to be resolved although the importance of the microstructure of the cement hydration process in relation to the macro properties of stabilized waste has been emphasized (2).

The aims of this study were therefore to identify the mechanisms operative in the fixation of hazardous heavy metal wastes by cement-based processes and also to improve the existing mix criteria of these cement-based processes.

APPROACH

The approach adopted in this study was to examine certain micro and macro properties of stabilized wastes using the techniques of: (i) X-ray diffraction (XRD), scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), and (ii) leaching tests and compressive strength tests. This paper reports the results of a study of an OPC/sodium silicate formulation although similar work is being undertaken by the authors at present on the alternative OPC/PFA process. Both these principal cement-based fixation techniques are being marketed in Europe and North America.

A simulated inorganic industrial waste containing Zn and Hg (both group IIb elements) was used in this study. These waste compounds were selected because of known industrial and experimental experiences which have indicated that their leaching potential is very different. The sample preparation varied according to the analytical procedure used and can be summarised as follows:

Leaching Test : A solution (200 ml of 2000 ppm) of Zn and Hg was solidified

by 50 g of OPC and 12 ml 40% Na_2SiO_3 , cured at room temperature for 28 days, crushed into small lumps and transferred to a container. Buffered acetic acid (100 ml of 0.15 M) was added and the mixture agitated using a rotational shaker. After 24 h, the slurry was filtered through a 0.45 μm membrane. A fresh portion of acetic acid was added and the process repeated over a period of time.

SEM, XRD and MIP : The composition of the four samples analysed by these techniques were as follows: Sample A = 10 g OPC + 10 ml H_2O ; Sample B = 10 g OPC + 10 ml H_2O + 1 ml 20% Na_2SiO_3 ; Sample C = 10 g OPC + 10 ml 2% Zn solution + 1 ml 20% Na_2SiO_3 ; Sample D = 10 g OPC + 10 ml 2% Hg solution + 1 ml 20% Na_2SiO_3 .

Samples were prepared by shaking either water or metal solutions with cement for 3 min in a plastic container; Na_2SiO_3 solution was then added as needed and the mixtures shaken for a further 30 s. All samples were allowed to cure at room temperature. For SEM and XRD studies 1-day samples were oven dried at 105°C for 15 min. Fracture specimens were prepared and coated with gold or carbon film prior to SEM examination using a Jeol 35CF + EDAX system (Energy Dispersive Analysis of X-rays) while powdered samples were analysed by a Philips Powder X-ray diffractometer. The porosity studies were performed on 7-day samples using a Carlo Erba Mercury Intrusion Porosimeter.

In addition, leached solidified waste samples (2000 ppm Zn and Hg) of every leaching period from a leaching experiment using 0.5 M

buffered acetic acid and a pre-leached solidified waste sample were oven dried at 105°C and examined by SEM. Powdered XRD patterns were obtained for solidified materials with and without dosage of Zn and Hg (at the 0.2% level) as before.

Strength Testing: Various mixes were prepared with different water to cement (W/C) and silicate to cement (Si/C) ratios. Additional mixes were prepared by using solutions containing 2% Zn and 2% Hg. Compressive strengths were tested at intervals of 1, 7 and 28 days using a standard compression test instrument conforming to BS 4550.

RESULTS

The results from the SEM, XRD, MIP and leaching studies of the four samples are summarized in Table 1 and Figure 1. The porosity data for the four sample types appear to suggest three basic distributions: one centered at 370 Å, one centered at 7500 Å, and the sum of these two. Such an interpretation is suggestive of at least two separate mechanisms operating in the interaction between these metals and the OPC/silicate system. Increased pore volume and pore size of the Zn-containing samples occurred because of the extensive growth of ettringite crystals in the hydrated paste due to the accelerated hydration of C_3A as observed in the SEM and XRD analyses. Despite the higher porosity the leachability of Zn is low which indicates that permeability is not an important factor in determining movement of this metal through the matrix and that chemical stabilization rather than physical encapsulation is the controlling factor in reducing metal mobility.

It has been claimed that stabilization of metal involves the formation of insoluble metal silicates but the SEM and XRD examination did not reveal any identifiable crystalline zinc silicate, though amorphous gel of calcium silicate was observed in both pure OPC/silicate and metal-dosed OPC/silicate matrices. Under these conditions it is thought likely that most of the Zn would be precipitated on the hydroxide or would react with the calcium hydroxide (C-H) to produce possibly calcium zincate (3) although no evidence of either of these zinc compounds has been found by the SEM or XRD tests. The absence of C-H crystals in the sample containing zinc indicates that C-H plays an important role in the fixation of Zn as confirmed by the semi-quantitative XRD study which demonstrated the presence of the more crystalline phases (Table 2). Indeed, a recent study on cementitious solidification of electroplating waste confirmed the presence of amorphous metal hydroxides in the solidified product (4).

By contrast, Hg did not seriously affect the normal hydration process as evident from the SEM, XRD and MIP studies. The formation of calcium silicate hydrates (C-S-H), calcium silicate and C-H all proceed in the same manner as in the OPC/silicate system which indicates that there is little or no interaction of this metal with OPC or sodium silicate. This inability of Hg to form an insoluble hydroxide or silicate with the solidifying material means that the metal remains in pore solution or at most is only loosely bound to the hydrated products through sorption. The metal is therefore physically encapsulated within the

TABLE 1. SUMMARY OF CORRELATION OF FOUR STUDIES

SAMPLE	SEM (1 day sample)		Powder XRD (1 day sample)		Porosimetry (7 days sample)	Total Pore Volume (cm^3/g)	Leachability Values
A. OPC + H_2O	C-S-H	fibrous	Unhydrated cement	medium strong	single	0.136	
	$\text{Ca}(\text{OH})_2$	large crystals	$\text{Ca}(\text{OH})_2$	strong		-	-
	ettringite	small rods	ettringite	weak	370A		
B. OPC/ Na_2SiO_3	C-S-H	fibrous, hydrated shell (Hadley grain)	Unhydrated cement	medium strong	double	0.416	
	$\text{Ca}(\text{OH})_2$	small crystals	$\text{Ca}(\text{OH})_2$	medium	370A	-	-
	ettringite	small rods	ettringite	weak	7500A		
	Ca-silicate gel	massive					
C. OPC/ Na_2SiO_3 + 2N Solution	C-S-H	a little, reticulated	Unhydrated cement	strong	single	0.684	
	$\text{Ca}(\text{OH})_2$	absence	$\text{Ca}(\text{OH})_2$	absence		low	low
	ettringite	large hexagonal prism with AFM	ettringite	medium	7200A		
	Ca-silicate gel	massive					
D. OPC/ Na_2SiO_3 + Hg Solution	C-S-H	fibrous, hydrated shell (Hadley grain)	Unhydrated cement	medium strong	double	0.376	
	$\text{Ca}(\text{OH})_2$	small crystals	$\text{Ca}(\text{OH})_2$	medium	370A	high	high
	ettringite	small rods	ettringite	weak	7500A		
	Ca-silicate gel	massive					

cement structure and not chemically stabilized to the extent observed for zinc. Mobilization of Hg leachability of the fixed product is high and probably dependent on the permeability of the solidified product.

The use of SEM has elucidated in what form this leaching fluid acts on the cementitious material (e.g. Figures 2, 3 and 4). In an unleached OPC/silicate sample with the simulated metal waste, normal hydration products of C-S-H, C-H, calcium aluminate hydrates (Aft and Afm phases) and unhydrated cement grains together with calcium silicate gel were observable. In comparison with OPC/silicate without metal addition, increased growth of the Aft phase with less C-S-H (Mostly Type I) was noticeable. The SEM study showed that the most

TABLE 2. SEMI-QUANTITATIVE XRD DATA

Sample	Phase	Relative Intensity*
A 50 g OPC	C-R	2.45
12 ml Na_2SiO_3		
200 ml H_2O	belite (C_2S)	1.03
	alite (C_3S)	0.87
B 50 g OPC	C-R	1.64
12 ml Na_2SiO_3		
200 ml 2000 ppm Hg,Zn	belite (C_2S)	1.16
	alite (C_3S)	0.95

* normalised to $\text{Hg}(\text{OH})_2$

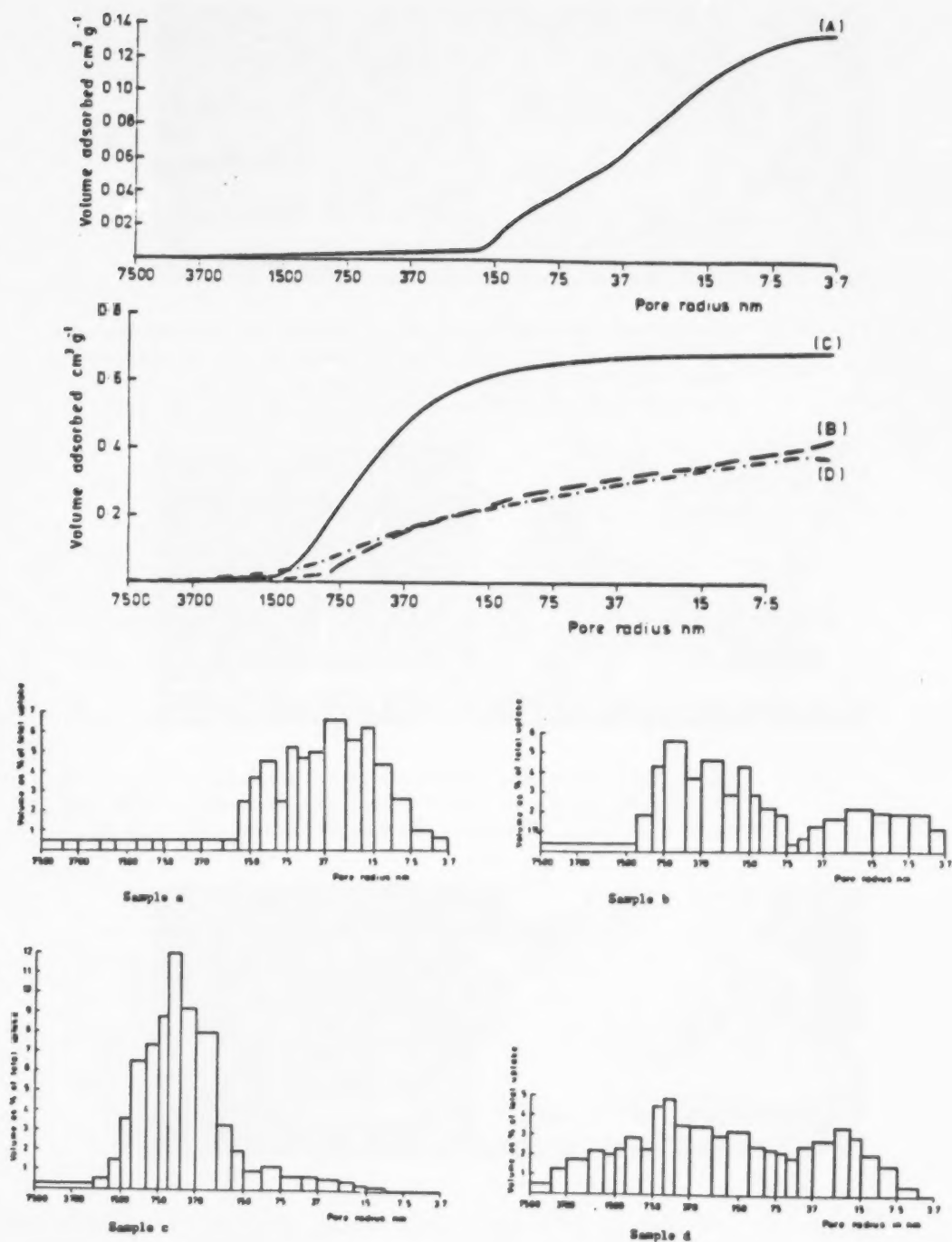


Figure 1. Cumulative pore volume and pore-size distribution.

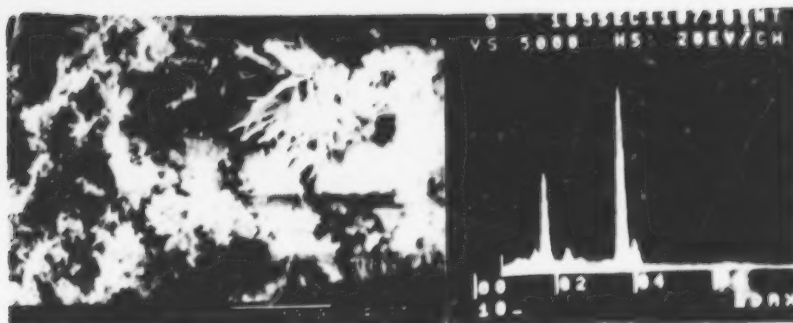


Figure 2. Micrograph showing pre-leached sample with long rods of ettringite, C-S-H, calcium silicate gel. Corresponding EDAX analysis showing major peaks at 1.74 and 3.69 ev (silicon and calcium respectively - more Ca than Si).

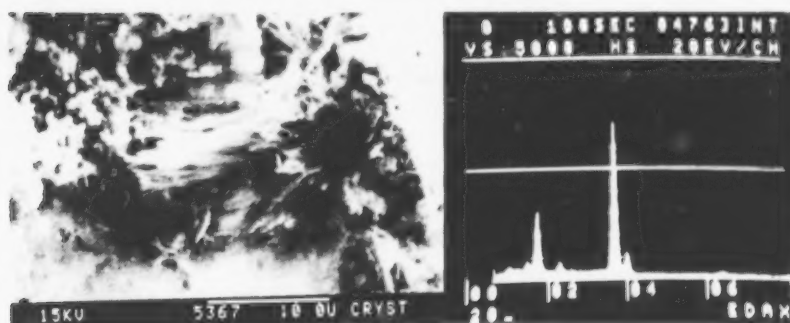


Figure 3. Micrograph of 1-day leached sample showing a grain with ettringite crystals and C-S-H. The structure of C-S-H is less defined. Sample still contains more Ca than Si.

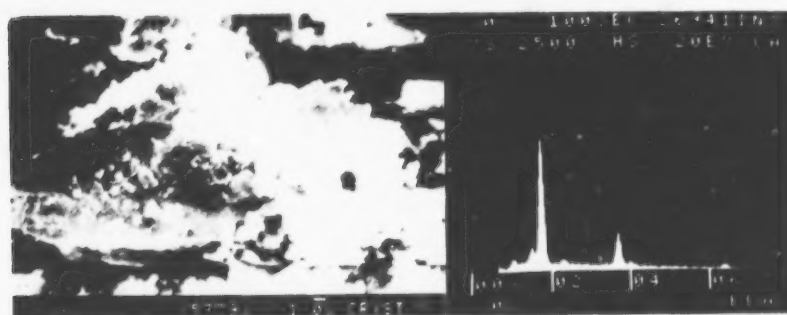


Figure 4. Micrograph of 5-day leached sample showing smooth hydrolysed surface of grain and areas of gel-like morphology. EDAX analysis indicates sample contains more Si than Ca.

easily hydrolysed structure was the C-S-H phase which after the 3 day leaching period was no longer observable. However Zn and Hg leachate concentrations did not change appreciably which indicates that C-S-H is unlikely to be involved in the fixation mechanisms.

Further leaching hydrolysed the matrix and was associated with continued Ca removal as demonstrated by the EDAX analysis. Possible sources of Ca are Aft and Afm, calcium silicate gel, C-H and unhydrated cement grains. After 3 days, less Aft (the most identifiable phase) and Afm were observable with increased calcium silicate gel type structures. Concentrations of Si and Ca were similar at this stage. However, the Aft phase was no longer visible after the 5 day leaching period and this coincided with the dramatic rise in Zn and Hg leachate concentrations which occurred subsequently. This indicates that the disappearance of this phase marks the beginning of break down of the structures that "fix" the metal though there is no direct evidence to prove that this phase is directly responsible for such fixation. After this phase was hydrolysed the cementitious matrix has been sufficiently broken down for the fixed waste material to be easily leached. This occurs after approximately 55% of Ca removal and corresponds to a massive breakdown of structure.

Figure 5 and 6 demonstrate that high Si/C ratios increase initial strength (within a few hours) but that the final strength is more dependent on the w/c ratio). The increase in w/c not only increases the total intruded volume but also

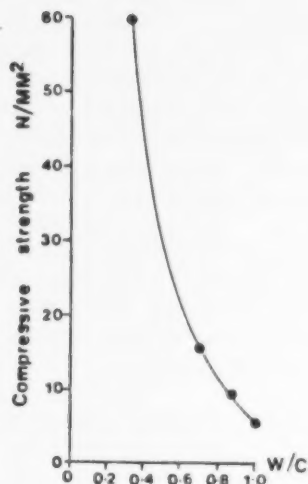


Figure 5. Strength vs W/C ratio.

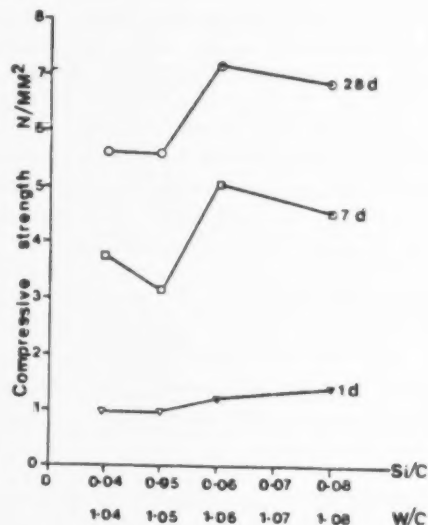


Figure 6. Strength vs Si/C and effective W/C ratios.

shifts the pore size distribution to a large pore radii. This is considered to be the most critical factor in determining the mechanical strength of a cementitious system (5). The role of sodium silicate in accelerating the setting of the product is crucial in normal stabilization practice in order to minimize runoff and leaching of waste material during the critical initial setting stage. The addition of sodium silicate does not promote a significant improvement in final strength which is in accord with the findings of Nelson and Young (6).

Material costs contribute the majority of the overall cost of solidification processes and thus to a waste disposer, the addition of additives such as sodium silicate which accelerate setting may increase the volume of waste that can be treated for the same amount of material. However, such an increase in the water content results in reduced physical strength which has important implications for the disposal of solidified wastes in landfill sites. It must be noted that the objective of these processes is to reduce both leachability and permeability and to improve compressive strength with minimal material costs.

ACKNOWLEDGEMENTS

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Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

SAMPLE	SEM (1 day sample)		Powder XRD (1 day sample)		Porosimetry (7 days sample)	Total Pore Volume ($\text{cm}^3 \text{g}^{-1}$)	Leachability Values	
A. OPC + H_2O	C-S-H	fibrous	Unhydrated cement	medium strong	single	0.136		
	$\text{Ca}(\text{OH})_2$	large crystals	$\text{Ca}(\text{OH})_2$	strong		-	-	
	ettringite	small rods	ettringite	weak	370A			
B. OPC/ Na_2SiO_3	C-S-H	fibrous, hydrated shell (Hadley grain)	Unhydrated cement	medium strong	double	0.416		
	$\text{Ca}(\text{OH})_2$	small crystals	$\text{Ca}(\text{OH})_2$	medium	370A	-	-	
	ettringite	small rods	ettringite	weak	7500A			
C. OPC/ Na_2SiO_3 + Zn Solution	C-S-H	a little, reticulated	Unhydrated cement	strong	single	0.684		
	$\text{Ca}(\text{OH})_2$	absence	$\text{Ca}(\text{OH})_2$	absence		low	low	
	ettringite	large hexagonal prism with AFm	ettringite	medium	7200A			
D. OPC/ Na_2SiO_3 + Hq Solution	C-S-H	fibrous, hydrated shell (Hadley grain)	Unhydrated cement	medium strong	double	0.376		
	$\text{Ca}(\text{OH})_2$	small crystals	$\text{Ca}(\text{OH})_2$	medium	370A	high	high	
	ettringite	small rods	ettringite	weak	7500A			
	Ca-silicate gel	massive						

SORBENT ASSISTED SOLIDIFICATION OF A HAZARDOUS WASTE

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ABSTRACT

Sorbent assisted solidification as discussed in this paper is a treatment technique for hazardous wastes containing toxic metals. The basis of the technique is adsorption/chemisorption of metals by a sorbent that is used in conjunction with a solidification process to immobilize metal contaminants. The sorbent-metal complex is thought to become incorporated (not simply entrapped) into the crystalline matrix provided by solidification processing.

Sorption isotherms and chemical leach tests were used to investigate the capacity of various sorbents to seize and hold metal ions, specifically copper ions. The sorbents investigated were flyash, soil, and organosilane conditioned flyash and soil. Organosilanes are chelating agents that have the ability to seize and hold metal ions. Adsorption isotherms were run in order to determine the ultimate capacity of the various sorbents for copper. The Langmuir equation was used to model the adsorption process. Desorption isotherms were run in order to obtain distribution coefficients related to the release of copper from solidified waste.

The data show that N-(β -aminoethyl)- γ -aminopropyl-trimethoxysilane, a commercially available organosilane, can be used to improve the adsorption properties of soil, and that sorbent assisted solidification reduces copper leaching. With the proper development and application, sorbent assisted solidification could provide the technology needed for improved land disposal of solidified hazardous waste.

INTRODUCTION

Solidification is a treatment technology that is sometimes applied to liquids and semi-solids which are too toxic for biological treatment, too low in energy value and/or too corrosive for thermal processing, and too dilute for landfilling. Solidification typically involves mixing a setting agent(s) with a waste to form a hard, durable product that is substantially insoluble in water and in which the waste contaminants are entrapped in the solidified mass. There are several commercially available solidification

processing systems in use in the United States (12). The most common setting agents are Portland cement and pozzolans such as flyash, kiln dust, lime, soluble silicates, gypsum, and combinations of these materials. (Pozzolans are materials other than Portland cement that have cementitious properties.) Generic descriptions of the commercially available solidification processes have been published by Malone and Jones (11).

Solidification typically provides three major advantages over raw waste disposal; these are 1) removal of free liquid, 2) development of

structural integrity, and 3) improved contaminant isolation and containment (11, 12, 14,). Isolation and containment of hazardous constituents are accomplished by waste entrapment in a cemented matrix and by conversion of waste constituents to less soluble compounds (precipitation). Unfortunately, these mechanisms do not always prevent the leaching of hazardous constituents. The effectiveness of the entrapment mechanism depends on the permeability and durability of the solidified product. Because waste constituents can interfere with the setting reactions responsible for the development of a hardened mass, there are problems with durability. Insoluble products from precipitation can be resolubilized if the leaching conditions are different from the conditions in which precipitation took place. In particular, pH and oxidation-reduction potentials can be altered by percolating water to resolubilize toxic metals. In addition, not all materials are insoluble under the pH and oxidation-reduction conditions in moist concrete or pozzolan. Hence, contaminants that have been simply entrapped or precipitated can be leached from solidified waste in varying degrees, depending on the type of waste and the kind of additives used (14).

Adsorption is one means by which soluble metals can be removed from contaminated aqueous systems (2,3,7,8). Since adsorption is reversible, desorption will occur to some extent depending on the relative affinity of the contaminant for the aqueous phase versus the sorbed phase. The thermodynamics of the sorption system partitions the contaminant mass between aqueous and adsorbed phases so that the contaminant is never all in one or the other phase, and thus, cannot be released all at one time. Consequently, the amount released and especially the release rate is

reduced if the contaminant is adsorbed to a solid phase, rather than simply entrapped in a lattice work as a soluble or potentially soluble salt.

Unfortunately, the solid matrix provided by cement and pozzolan processing has little or no sorption potential. However, if a sorbent that becomes incorporated into the crystalline matrix provided by solidification is included in the process formulation, then the pollutant potential of the solidified waste should be significantly reduced.

The metal sorption properties of materials can be improved by bonding certain organosilanes to them (9, 13). Organosilanes are silicon compounds derived from silane, SiH_4 . As chelating agents some organosilanes have the ability to seize metal ions and sequester them from further reactions. Leyden and Luttrell (9) used the metal chelating properties of organosilanes to preconcentrate dissolved metals prior to chemical analysis by X-ray fluorescence. Malone and Karn (13) reported the usefulness of an organosilane-silica gel sorbent in removing cadmium, chromium, copper and zinc from contaminated wastewater.

PURPOSE

The objective of this study was to investigate the feasibility of reducing the metal leaching potential of solidified waste by conditioning of selected solidification additives with N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane.

APPROACH

The research approach consisted of 1) conducting adsorption isotherm tests on organosilane-additive preparations in order to determine the sorption characteristics for copper and 2) conducting desorption isotherm

tests on solidified waste prepared with and without silane conditioning of selected solidification additives in order to obtain distribution coefficients for copper release.

Waste Solidification

A concentrated brine containing approximately 12 percent by weight chloride, 8 percent by weight organic carbon, 17 percent by weight dissolved solids, 4040 mg/l copper, and various toxic substances such as aldrin, arsenic, and cyanide at parts per million levels was collected from a hazardous waste impoundment for study and testing. The liquid was solidified in 1 liter batches with equal weights of soil, flyash, lime, and waste. This solidification process was chosen for investigation because it included two materials with sorbent potential (soil and flyash). The flyash was obtained from a local power plant. The ash had a specific gravity of 2.07 and contained 4.7 percent lime as CaO. The soil, also available locally, was a sandy clay (CL by the Unified Soil Classification System). The solidified waste was cured at room temperature for 7 days prior to testing.

Sorbent Preparation

The preparation of sorbents involved the bonding of N-(β -aminoethyl)- γ -aminopropyltrimethoxysilane to either flyash or soil. The organosilane (Dow Z-6020) was obtained from SCM Speciality Chemicals, Gainesville, Florida. The bonding procedure adapted from Leyden and Luttrell (9) incorporated the following steps:

a. A 10% aqueous silane solution was prepared by adding silane to deionized-distilled water with stirring. The solution was acidified to pH 5-6 by adding reagent grade glacial acetic acid. The pH was checked with pH paper. Plastic containers were used to avoid reaction with glass.

b. One gram of either flyash or soil was contacted with aqueous silane on a mechanical shaker for 30 minutes at a liquid to solids ratio of 1.5 ml of aqueous silane to one gram of substrate.

c. The mixture was reacted at 70°C in a vented oven for 24 hours. In one bonding procedure the loss of water was controlled so that the mixture was not allowed to dry. In another the mixture was taken to complete dryness at 70°C.

d. The sorbent preparations that were taken to complete dryness were washed with water to remove excess silane and then dried at 40°C.

e. The sorbent preparations that were not taken to complete dryness at 70°C were washed with water to remove excess silane and then air dried in a hood at room temperature.

Adsorption Isotherms

Adsorption isotherms were run in order to determine the ultimate capacity of the various sorbents for copper and to determine equilibrium adsorption constants. In these tests one gram quantities of sorbent were contacted on a mechanical shaker for 24 hours with 100 ml of liquid waste in various dilutions. Each mixture was then filtered and analyzed for copper. Six dilutions of liquid waste were used as follows: 1000/1, 100/1, 50/1, 10/1, 5/1, and 1/1 (no dilution). Blanks consisting of sorbent and deionized water were run with each adsorption isotherm test. Liquid-solid separation was by filtration using Gelman No. 61631 glass fiber filters. Adsorption isotherms were run on soil, soil with organosilane, flyash, and flyash with organosilane.

Desorption Isotherms

Desorption isotherms were run by contacting solidified waste samples

with deionized-distilled water on a mechanical shaker for 24 hours in liquid to solid ratios as follows: 50 ml:5g, 50 ml:2g, 50 ml:1g, 100 ml:1g and 100 ml:0.5g. The mixtures were filtered and analyzed. Blanks consisting of deionized-distilled water were included in each set. Liquid-solids separation was by filtration using Gelman No. 61631 glass fiber filters. Desorption isotherms were run on waste solidified using soil without organosilane conditioning and on waste solidified using organosilane conditioned soil.

Chemical Analysis

Isotherm samples (aqueous phase) were analyzed for copper on a directly-coupled plasma arc spectrophotometer by the Analytical Laboratory Group (ALG), Environmental Laboratory, USAE Waterways Experiment Station, Vicksburg, MS.

PROBLEMS ENCOUNTERED

The most significant problem encountered involved the soil/organosilane bonding procedures. When the soil organosilane mixture was not taken to dryness, the sorbent produced was inferior to that produced when the mixture was taken to dryness. This was indicated by reduced adsorption coefficients as discussed in the results section. One possible explanation for this relates to the collision frequency between the silane molecules and active hydroxyl sites on the soil surface. The reaction of organosilane with a substrate involves hydrolysis of the methoxy groups, polymerization by condensation, hydrogen bonding between the condensed organosilane polymer, and finally formation of a silicon-oxygen bond (siloxane) between the substrate and the silane (1). Apparently the final step is not accomplished until condensed organosilane polymer and active sites on

the soil surface are forced into a high collision probability by taking the mixture to dryness.

RESULTS

Adsorption Isotherms

In an isotherm test the amount of contaminant removed is determined as a function of the aqueous concentration at a constant temperature. The resulting set of data is called an adsorption isotherm. From the data a table of aqueous phase concentrations, C , and corresponding sorbent phase concentrations, q , can be prepared.

The Langmuir equation is often used to model adsorption processes at equilibrium (15). The Langmuir equation is

$$q = K_d Q C / (1 + K_d C) \quad (1)$$

where

q = Concentration of contaminant in the adsorbed phase, m/m_s

Q = Ultimate monolayer capacity of the sorbent, m/m_s

C = Concentration of contaminant in the aqueous phase, m/L^3

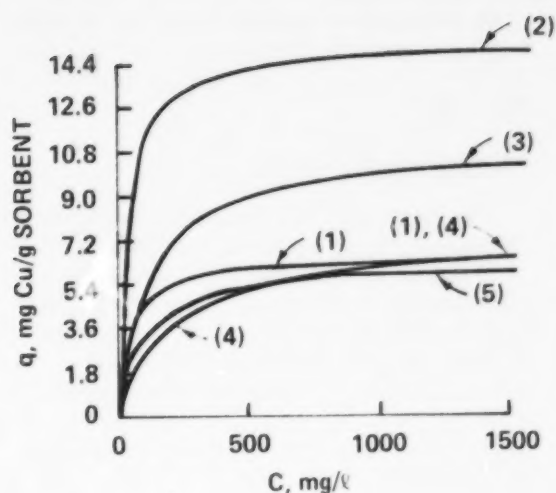
K_d = Langmuir distribution coefficient, L^3/m

m_s = Mass of sorbent

The adsorption isotherm data obtained in this study were analyzed by least squares fitting of the data to the linear form of equation (1) below.

$$C/q = 1/(QK_d) + C/Q \quad (2)$$

The coefficients $1/(QK_d)$ and $1/Q$ were determined by least squares analysis and from these Q and K_d were obtained. These coefficients were then used to produce the adsorption isotherms shown in Figure 1.



LEGEND

- (1): SOIL
- (2): SOIL/ORGANOSILANE TAKEN TO DRYNESS
- (3): SOIL/ORGANOSILANE, WET
- (4): FLYASH/ORGANOSILANE TAKEN TO DRYNESS
- (5): FLYASH

Figure 1. Adsorption Isotherms

The curves show that conditioning of the soil with organosilane enhanced the ultimate adsorption capacity, Q . (Q is the value each curve asymptotically approaches.) On the basis of ultimate adsorption capacities, the organosilane conditioned sorbents were superior to the unconditioned sorbents, and the soil based sorbents were superior to the flyash based sorbents. The adsorption isotherm data also show that the soil even without organosilane conditioning is more than just a filler in the solidification process. Copper is adsorbed by the soil.

The data also indicate that the soil/organosilane bonding procedures affects sorbent performance. The best copper adsorbent investigated

in this study, as indicated by the isotherms shown in Figure 1, was the soil/organosilane sorbent prepared by taking the soil/organosilane mixture to dryness. Soil was generally less effective than the soil/organosilane sorbents, especially when the soil/organosilane mixture was taken to dryness during sorbent preparation. The flyash based sorbents were inferior to the soil based sorbents. The poor performance of the flyash preparations was probably due to the lime component in the flyash. Base hydrolysis of the siloxane bond can occur under certain conditions (1).

Desorption Isotherms

Desorption isotherms can be used to provide fundamental information on the interactions between groundwater and contaminated soils and sediments (4, 5, 16). If the sorption processes of adsorption and desorption have taken place under identical conditions, then the desorption of a contaminant back into the aqueous phase should proceed down the adsorption isotherm and follow it exactly. However, the conditions under which adsorption takes place is usually significantly different from those under which desorption isotherms are developed. If the sorption systems differ significantly in pH, ionic strength, and chemical activity, the desorption process will not simply be a reversal of the adsorption process.

Jeffe and Ferrar (6) suggested the following simple mass action desorption model:

$$dC/dt = -K'_1 C + K_2 q \quad (3)$$

where K'_1 is the adsorption rate and K_2 is the desorption rate.

For steady state conditions $dC/dt = 0$, and equation 3 becomes equation 4 below:

$$q = K'_d C \quad (4)$$

where $K'_d = K'_1/K_2$.

Equation 4 describes the relationship between sorbed and aqueous phase concentration for a desorption-dominated equilibrium by a simple distribution coefficient, K'_d . Each value of contaminant loading in the solid phase, q , supports a unique aqueous phase concentration, C , that at equilibrium is directly proportional to q by the distribution coefficient, K'_d . In terms of leaching potential, the higher the distribution coefficient, K'_d , the lower the aqueous phase concentration, C , that a given sorbent loading, q , will support.

The desorption isotherm data are presented in Figure 2. Sorbed versus aqueous phase concentrations are plotted for waste solidified using soil without organosilane conditioning and for waste solidified using soil with organosilane conditioning. The desorption isotherm data fit the linear model of q versus C presented in equation (4). The desorption isotherms show that sorbent assisted solidification using organosilane conditioned soil produced a product with a higher K'_d than did sorbent assisted solidification using soil alone. The affinity of copper for the organosilane reduced the amount of copper in the aqueous phase. The organosilane used in the desorption isotherm test was not prepared by taking the soil/organosilane mixture to dryness. The adsorption isotherms in Figure 1 indicate that had sorbent preparation involved taking the soil/organosilane mixture to dryness, the distribution coefficient would have been even higher. The problem with bonding procedures was not recognized early enough in the testing program to include sorbents prepared by taking the mixture to dryness in the desorption isotherm testing.

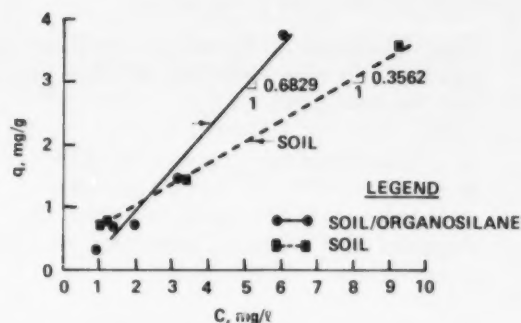


Figure 2. Desorption Isotherms

Potential For Field Application

Several important aspects of field application were not addressed in this laboratory study of sorbent assisted solidification using organosilane. Topics beyond the scope of the investigation include scale-up factors, organosilane compatibility with alternative binder/substrate systems, long-term stability of the solidified product, and engineering economy. Additional testing and evaluation is needed before organosilane assisted solidification can be applied in the field.

In addition, organosilanes are produced as specialty chemicals that are expensive in small quantities. Even with a significant cost breakthrough between laboratory and bulk quantities, full-scale application of sorbent assisted solidification using organosilane may be limited to small volumes of highly contaminated metal wastes that would otherwise pose a serious environmental hazard if landfilled.

CONCLUSIONS

Sorbent assisted solidification using organosilane is an innovative treatment technology that could be applied, depending on technical and economic factors associated with full-scale application, to highly contaminated metal wastes prior to

land disposal. Specific conclusions drawn from the results of the study are as follows:

1. Organosilane, specifically N-(β -aminoethyl)- γ -aminopropyl-trimethoxysilane, can be used to improve the natural adsorptive capacity of soil for copper.
2. Organosilane, specifically N-(β -aminoethyl)- γ -aminopropyl-trimethoxysilane, can be used to reduce the copper leaching potential of solidified waste when organosilane conditioned soil is used as a solidification additive.
3. Soil/organosilane bonding procedures affect sorbent performance. When the soil/organosilane mixture is not taken to dryness during preparation, the sorbent produced is inferior to that produced when the mixture is taken to dryness.

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THE EFFECT OF PARTICLE SIZE ON THE LEACHING OF HEAVY METALS FROM STABILIZED/SOLIDIFIED WASTES

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ABSTRACT

Stabilization/solidification of hazardous liquids and sludges by a variety of techniques has been investigated as a method of treatment that will bind hazardous materials in a form that minimizes adverse effects on the environment after landfilling. One method of stabilization/solidification that has been investigated is the combination of the waste with portland cement to form a cement paste. The structure of the paste resists chemical attack, making the technique attractive as a disposal alternative for heavy metal sludges. This paper presents results concerning the effect of particle size on the leaching pattern of metals from these wastes. Both batch and upflow column leaching tests were investigated.

The results indicate that in the early part of the column test, small particles at the bottom of the column release both metals and alkalinity. As the leachant moves upward through the column, the alkalinity leached neutralizes the acid leachant causing the pH to rise. This forces the metals that were leached below to either be re-precipitated or sorbed onto a particle surface. As the leaching zone rises through the column, metals are concentrated near the top of the column. When the leaching zone breaks through the top of the column, metal concentrations in the leachate increase rapidly. As the extraction continues beyond this point, the concentrations of metals in the leachate gradually decline. In the columns packed with larger particles, however, the rate of alkalinity release from the particles is not rapid enough to neutralize all the acid in the leachant by the time the leachant reaches the top of the column. This results in an immediate release of metals into the leachate. As extraction continues, the rate of metals release gradually increases, indicating that the alkalinity that is being released is exposing more surface area to the acid leachant.

INTRODUCTION AND PURPOSE

The disposal of hazardous waste on land has almost universally led to environmental problems due to leaching of waste constituents into groundwater. Properly designed, constructed and managed "secure" chemical landfills, in which clay or synthetic membrane liners and leachate collection systems are used, can delay the onset of groundwater contamination, but these liners may eventually break down.

One method of disposing of some of these wastes in a more environmentally acceptable fashion is to stabilize/solidify them before landfilling. In this process the waste sludges are combined with various additives that both chemically bind and physically solidify the hazardous materials, thus making them less susceptible to leaching. Stabilized/solidified wastes may still leach with time, but the rate of leaching should be very low so that the pollutants will disperse into the

environment without adverse consequences.

One method of stabilization/solidification which has been studied extensively at the University of New Hampshire consists of the combination of inorganic waste sludges with portland cement to form a cement paste. The structure of the Solidified paste resists physical attack and gives the product strength and durability, and the highly alkaline nature of the material resists chemical attack, making the technique attractive as a disposal alternative for heavy metal sludges.

The environmental acceptability of hazardous wastes is partially determined by use of the U.S. Environmental Protection Agency Extraction Procedure (EP) test, in which the waste is contacted with a mild acetic acid leachant for 24 hours, after which the leachant is analyzed for specific metals which may have leached. This test procedure is not valid, though, for stabilized/solidified wastes because the alkalinity present in the waste quickly neutralizes all of the acid present so that leaching occurs under highly alkaline conditions rather than acidic ones, and because the solidified waste is a monolithic mass rather than in particulate form. These properties are beneficial from the standpoint of environmental protection as they greatly decrease the tendency of the material to leach, but they do cause problems relative to determining the actual leachability of the waste. Difficulties associated with the alkaline nature of the waste are addressed elsewhere (1,3,4,7). This paper is concerned with the effect of particle size on leaching properties of solidified/stabilized hazardous wastes.

Stabilized/solidified wastes are placed in the environment as monolithic blocks with low permeabilities. Over time, though, these blocks may be physically and chemically attacked in such a way as to create smaller particles. It has been proposed that the amount of metals leached should be directly proportional to the surface area available for leaching (5,6,8). Early research at the University of New Hampshire, though, found that smaller particles leached less metals than larger particles (2).

The purpose of this paper is to evaluate this phenomenon and to explain how particle size affects the release pattern of heavy metals from stabilized/solidified hazardous wastes during the conduct of both batch and column extraction tests.

APPROACH

Synthetic hazardous waste sludges were prepared in the laboratory, solidified/stabilized with type II portland cement, ground to specified size ranges, and the ground material subjected to various leaching tests. Batch extractions were performed using both the U.S. EPA EP Toxicity test procedure (9) and a modified test developed by Bishop et al. (2). Column extraction test procedures were developed by the authors.

The sludges were formulated to contain 0.04 moles/L each of cadmium, chromium, and lead. Metals were added as chromium chloride, cadmium nitrate and lead nitrate and converted to their hydroxide precipitate forms in the sludge by neutralization of the solution to pH 8.5 with sodium hydroxide. The sludges were mixed with type II portland cement to form cement pastes with water/cement (w/c)

ratios of 0.5 and 1.0 using ASTM procedure C30582. The freshly mixed pastes were placed in 3.8 cm diameter by 7.6 cm tall PVC cylinders and allowed to set for 24 to 48 hours at 100% humidity before they were removed from their molds and returned to the 100% humidity environment.

Cylinders to be used in the extraction tests were broken and pulverized with a mortar and pestle. The particles were mechanically sieved and the resulting particle sizes were collected for testing. Particle size ranges used were 4.8-9.5 mm (large particles) and 0.3-0.6 mm (small particles).

Batch extraction of the particle fractions were performed using the U.S. EPA-EP toxicity test and a modified version developed in our laboratories. The two main differences in these tests are: 1) The EP-toxicity test uses 0.5N acetic acid to enhance leaching while the modified test use 17.4 N glacial acetic acid, and 2) the EP-toxicity test limits the amount of acid added to keep the pH at 5.0 ± 0.5 to 40 ml so that the actual pH of the leaching medium may be well above pH 5.0, while there was no limit to how much 17.4 N acetic acid could be added to keep the pH at 5.0 ± 0.5 in the modified test. The samples were placed on a shaker table in a controlled temperature room (20°C); the pH was monitored and adjusted over a 24 hour period as specified in the EP-toxicity test procedure (9).

The samples were removed from the shaker table after 24 hours and filtered through a

0.45 μ m filter. Metal analysis was performed on the filtered leachate by atomic absorption spectrophotometry.

Column leaching tests were performed in the upflow mode. The columns were 46 mm diameter by 139 mm high Buchner type funnels that were modified by a glassblower. The modifications included addition of a side arm for effluent flow and tapering the neck of the funnel to a pipet-like tip to accommodate narrow bore tubing.

All leachant flows were set at 0.2 ml/min. Acid strengths of 0.05N and 0.1N were used to create acid fluxes of 1.0 and 2.0 meq/g sample/day. Leachates from the columns were collected in 500 ml Erlenmeyer flasks. Leachate was collected every 24 hours, pressure filtered through a 0.45 μ m filter, and the metal concentrations determined. The alkalinity of the leachate was measured with a recording titrator.

RESULTS AND DISCUSSION

The results of batch leaching tests for cadmium using the modified EP procedure are presented in Figure 1. Leachate lead concentrations followed similar patterns. Leachate metal concentrations in the EPA-EP extracts were much lower, being at or near minimum detection limits. The pH of these leachates were generally between 10 and 11, considerably higher than in the modified EP leachates. Thus, little of the metal in the samples subjected to the EPA-EP test was in a soluble form.

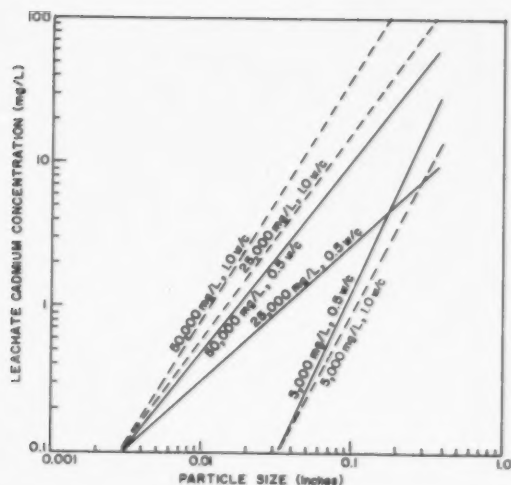


Figure 1. Effect of Particle Size, Water: Cement Ratio and Sludge Concentration on Cadmium Leaching - Batch Tests.

It was initially hypothesized that as the particle size decreased, thereby increasing the surface area, the magnitude of metal leaching would increase. Surprisingly, the reverse of this was found to occur. This led to the question as to whether the heavy metals are actually "locked up" in the smaller particles or whether some other property of the smaller particles enhances metal binding. Total digestions were performed on representative particles of each size range using boiling nitric acid. These indicated that heavy metal concentrations were the same in all particle sizes before leaching. One explanation for these results is that the heavy metals are bound to the particles by sorption mechanisms. Increased surface areas occurring in the smaller particles would cause greater ion exchange and adsorption of heavy metals and thus lower leach-

ate metal concentrations.

Column leaching tests were then developed to investigate this phenomenon further. It was observed that as the extractions proceeded, the small size particles that were exposed to the acid turned from their natural cement-gray color to a dark gray and then to an orangish-brown color and finally to a white color. By observing the boundary between the cement gray and the dark gray, the progression of the acid attack could be closely monitored. The larger particles also turned an orangish brown, but never turned to the white color of the smaller particles. The progression of acid attack in the columns containing large particles was faster than in columns with small particles. All the large particles turned to an orangish brown color in the first two days of extraction, while the color change of the small particles was a slower progression up through the column.

The difference in behavior of the large and small particles may be explained by the difference in available surface area. The small particles have more available surface to leach alkaline species from, neutralizing the acidity of the leachant before it reaches the particles near the top of the column. The large particles, on the other hand, do not have as much available surface alkalinity and the acid attacks the entire column without being completely neutralized. In all cases, the time of break through of the orange front at the surface of the layer of particles corresponded to the time when the pH of the leachate dropped below 6, and to the time when the ratio of total alkalinity leached from the particles to the total amount of acid passed through the column fell below 1.0. This is the point at which the acid being

added is no longer being completely neutralized by the alkalinity of the cement paste.

Figure 2 shows the concentrations of metals leached from the particles as a function of the total amount of acid passed through the column for one experimental run. The release of metals into the leachate water leaving the columns containing small particles did not occur until after addition of approximately 8 meq acid/g waste.

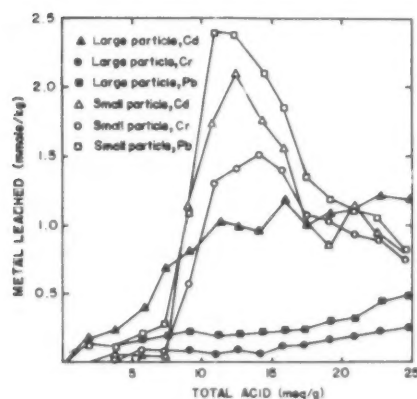


Figure 2. Metals Leached as a Function of Total Acid Added - Column Tests.

Metal concentrations in the leachate then increased rapidly for a time before falling back to lower concentrations. The rapid rise in concentrations corresponded to the time when the ratio of alkalinity leached/meq of acid passed through the column fell below 1.0 (Figure 3), indicating the time when the alkalinity leached from the solid could no longer neutralize all of the acid being added. The period of declining concentrations is probably due to a bulk diffusion

limited release, which would predict similar declining rates of release as time progresses since it takes more time for ions to

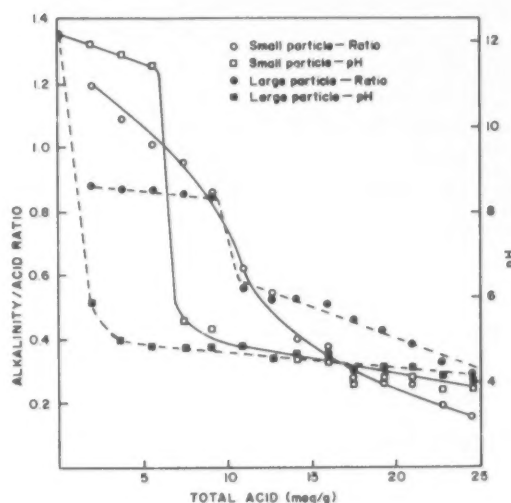


Figure 3. Alkalinity Leached to Acid Added Ratios - Column Tests.

diffuse from further within the particle.

The metal leaching patterns for large particles, shown in Figure 2, were quite different than those for the small particles. The release of metals from the large particles began immediately and concentrations increased throughout the test, with only a slight decrease near the end of the test. Cadmium appeared to leach much more readily than chromium or lead. This rise in metal release could be a direct function of surface area available for leaching. As alkalinity is leached from the particles, more pores are opened, leading to additional surface area available for acid attack and metals release. Alkalinity leached/acid added ratios were always below 1.0 (see Figure 3) indicating that sufficient alkalinity to neutralize acid was not immediately available to the leachant due to the reduced surface area provided by larger particles. As

a result, the pH of the leachant remained low, allowing any metals leached to remain in solution.

Figure 4 shows curves of alkalinity leached as a function of acid

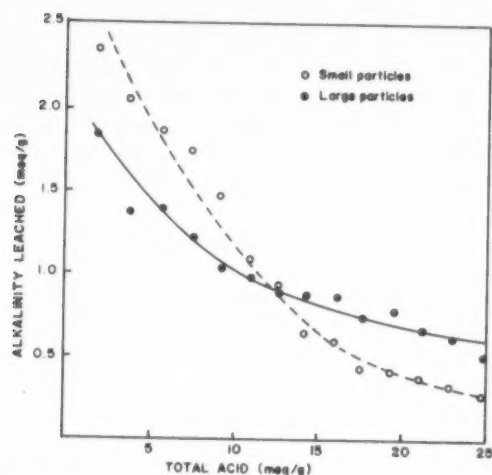


Figure 4. Alkalinity Leached Function of Total Acid Added - Column Tests.

passed through the column for both small and large particle columns. The rate of alkalinity leaching from the large particles dropped as the extraction progressed, but not as rapidly as that from the small particles. This indicates that the available surface area for leaching was increasing at a decreasing rate, which corresponds with the metal releases.

These results are in general agreement with those presented earlier for batch leaching tests, where it was found that smaller particles leached less metals than larger particles, particularly for low acid doses which would correspond to conditions in the batch tests. However, plots of cumulative metals leached as a function of total acid

addition (Figure 5) indicate that eventually cumulative metals leached from the small particles becomes greater than from the large particles. This generally occurs at the point at which the acid flowing by the small particles is no longer totally neutralized and leachate pH drops.

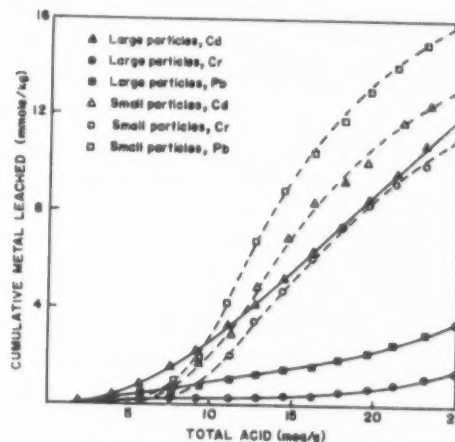


Figure 5. Cumulative Metal Leached as a Function of Total Acid Added - Column Tests.

Chromium and lead were leached in much higher concentrations from the small particles than from the large particles. The cement matrix in the small particles was probably breaking down due to the lack of alkaline species available to neutralize the acids containing them. If the chromium and lead were bound into the cement matrix, the higher rate of leaching from the small particles would be explained. To determine whether the cement matrix of the small particles was actually being broken down at a higher rate than for the larger particles, representative samples were analyzed for silicon. These analyses showed that the smaller particles released three times as much silicon as the large particles after the initial alkalinity was reduced.

Figure 6 shows a pC-pH diagram for hydroxides for lead, cadmium, and chromium. Higher pC values mean less metal in the soluble phase since pC is the negative logarithm of the concentration.

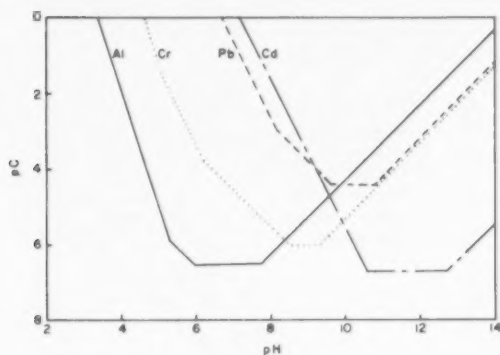


Figure 6. pC-pH Diagram for solubility of Metal Hydroxides.

The high pH of the paste as it is being mixed (around pH 12) causes lead and chromium to form soluble hydroxide complexes. Availability of these anions in solution allows them to participate in the formation reactions, possibly much like aluminum. The insoluble cadmium hydroxide is not available to take part in solution reactions and is trapped in the pores as the solid is formed. This could explain why leachability of chromium and lead appears to be dependent on the dissolution of the silicate matrix while release of cadmium seems to occur as pores are opened. Although the curve shows that only about 10% of the chromium and lead originally present would form the anionic hydroxide complex, more could be formed as that initially present is depleted by participating in solid formation reactions. The hypothesis cannot rule out the possibility of an encapsulation type reaction where lead and chromium hydroxide are

surrounded by the silicate fibrils that are formed. However, there is no apparent reason why encapsulation would occur for chromium and lead and not for cadmium.

The results of the column tests indicate that cadmium is primarily bound into the solid matrix by surface related mechanisms such as ion exchange and adsorption. The lead and chromium, however, are primarily bound into the silicate matrix of the paste.

The size of the particles being leached controls the extent to which acidic leachant is neutralized in the beginning of the extraction, with small particles having more alkalinity immediately available. When the leachant is neutralized, metal concentrations in the leachate are low. However, when the leachate can no longer be neutralized because much of the available alkalinity has been leached, the metal concentrations in the leachate increase. The small particle size leached more metal than the larger size, but release was delayed by the particles' ability to neutralize the leachant before it left the column in the early part of the extraction.

The small particles in the lower portions of the column began to dissolve early in the extraction, as buffering capacity of these particles was quickly reduced. The rapid reduction of buffering capacity was due to immediate availability of alkaline species from the large exposed surface area. This dissolution of the small particles led to the release of lead and chromium in higher concentrations than were observed in the large particle leachates where alkaline species available from deeper within the particles pre-

vented dissolution from occurring as rapidly. Final cumulative cadmium concentrations and total alkalinity leached from large and small particles were similar. The similarity in alkalinity leached indicates that approximately the same amount of surface area had been exposed to the leachant by the end of the extraction. This led to nearly equal amounts of cadmium leached, since the cadmium is primarily bound to the surface or held as insoluble hydroxides in the pores.

It is apparent that batch leaching tests or short duration column tests do not provide a true indication of the leaching potential of solidified/stabilized hazardous wastes or of the metal binding mechanisms present. It is only through the use of longterm column leaching tests or possibly with multiple extraction batch leaching tests that meaningful data can be obtained.

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DEVELOPMENT OF A METHOD FOR MEASURING
THE FREEZE-THAW RESISTANCE OF
SOLIDIFIED/STABILIZED WASTES

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ABSTRACT

A description is given of the development of a method for measuring the freeze-thaw resistance of solidified/stabilized wastes. Various features of the existing ASTM methods have been adopted, such as the use of weight loss as a measure of freeze-thaw resistance, and the media and durations of the freezing and thawing phases. New features are also introduced, including loose particulate removal method and the use of control specimens to isolate the effect of freezing and thawing.

The initial results show that a relative standard deviation (ratio of standard deviation to mean) of better than 17% could be obtained in the cumulative weight loss measurements. The method was applied to a synthetic waste treated with five different additives that are commonly used in solidification/stabilization processes. Differences in freeze-thaw resistance could be readily observed, thus indicating the potential use of the method for comparing different processes on the basis of freeze-thaw resistance.

Modification to simplify the method are suggested, and further tests are planned to assess its applicability to a wide variety of wastes treated by commercially used processes. Adoption of the method for measuring wet-dry resistance will also be assessed.

INTRODUCTION

Leaching of contaminants from land-disposed wastes is a well recognized environmental concern. To reduce such leaching and its consequent potential for ground-water contamination, solidification/stabilization (s/s) processes are widely used to treat wastes prior to disposal. Typically, aqueous wastes containing heavy metals are treated in this manner.

In brief, s/s processes involve the use of additives to convert a liquid waste into a solid monolithic-matrix. The contaminants, which are then contained within such a matrix, will therefore become less accessible to potential leaching agents. In some cases, the additives are selected to also react with and reduce the solubility of the contaminants.

Hence, an additional measure is provided to further reduce the potential for groundwater contamination.

Clearly it is important that the physical integrity of such treated wastes be maintained. Disintegration, resulting in generation of small particulates, or formation of cracks, thereby increasing the apparent permeability of the solid matrix, would defeat the purpose for which s/s processes are used.

Such deterioration in physical integrity could be caused by adverse climatic conditions, such as changes in temperature which cause repeated freeze-thaw cycles. Even if the treated wastes are eventually buried under soil layers, which would minimize such effects, there is still an intermediate period during which these wastes are exposed to such adverse conditions. Therefore, at locations where freezing and thawing occur, measurements of ability to withstand these conditions are an important and integral part of s/s process evaluation.

This paper describes the development of a new method for quantifying the freeze-thaw resistance of solidified wastes on the basis of weight loss measurements.

EXISTING METHODS

To our knowledge, there are only two existing methods for measuring freeze-thaw resistance. Both are ASTM standard methods, developed for concrete and

soil-cement mixtures. These are briefly described as follows:

ASTM C 666-80, "Resistance of Concrete to Rapid Freezing and Thawing"¹

The test specimens are prisms of 10 x 10 x 38 cm nominal dimensions, which are immersed in water at 4.4°C during the thawing phase. For the freezing phase, one of two procedures could be adopted. In Procedure A, the test specimens remain in the water used in the thawing phase, and in Procedure B, they are exposed to air. In both cases, the freezing phase temperature is -18°C.

Several constraints are imposed on the duration of the transition period, on the rate of temperature change during this period, and on the minimum duration of the thawing phase relative to that of one freeze-thaw cycle. However, strict requirements are not specified for the freezing and thawing periods. Test specimens could be stored in a frozen condition "indefinitely" when interruptions occur.

The freeze-thaw resistance is expressed as durability factor (DF), ranging from 0 to 100, which is computed from measurements of dynamic modulus of elasticity. These measurements are carried out at least once every 36 freeze-thaw cycles.

The prescribed number of freeze-thaw cycles is 300, or that when the dynamic modulus elasticity reduces to 60% of the initial value. The acceptable, within-laboratory precision values are specified in terms of standard deviation and actual difference in

individual DF values. These vary depending on the average DF: in the range of 1-15 in standard deviation and 2-43 in difference between test results.

This method was applied to samples of Uranium mine-mill tailings treated by a number of s/s processes.² Experimental difficulties were encountered, such as surface scaling, sample disintegration and warping, and difficulties in carrying out quantitative measurements were reported. From visual observations, however, the different processes were ranked in terms of freeze-thaw resistance.

ASTM D560-57 (Re-approved 1976).
"Freezing and Thawing Tests of
Compacted Soil-Cement Mixtures" 3

The test specimens are cylindrical, with nominal dimensions of 10 cm diameter and 12 cm long. Both the freezing and thawing are carried out in air, with 100% relative humidity and at temperatures of -23°C and 21°C, respectively. The freezing and thawing periods are specified at 24 h and 23 h, respectively. As in the previous method, during interruptions, test specimens are stored in a frozen condition.

The freeze-thaw resistance is expressed in terms of weight loss. Measurements of weight loss involve the application of "firm strokes" on all surface areas of the test specimen with a wire scratch brush. A firm stroke is defined to correspond to approximately 13.3 N (3 lbf) as measured with a balance. For specimens that form scales, a sharp-pointed instrument such as an ice pick is to be used

instead of a brush. These weight loss measurements are usually made after each freeze-thaw cycle.

The prescribed number of freeze-thaw cycles is 12. No specification is given on the acceptable precision value for the weight loss measurement.

This method was applied to four treated wastes with different types of physical characteristics: low-strength concrete, rubber-like solid, plastic-encased block and soil-like material.⁴ With the exception of one plastic-encased sample, all samples disintegrated after 12 freeze-thaw cycles. In fact, 62% of the samples disintegrated after 2 cycles. The weight loss measurement results were not reported.

DESCRIPTION OF PROPOSED METHOD

Various features of the existing ASTM methods have been adopted. These include:

(1) Test specimens are frozen in air and thawed in water (C666-80, Procedure B).

(2) The freezing and thawing periods are 24 ± 1 h, and the maximum number of freeze-thaw cycles is 12. The freezing and thawing temperatures are $-20 \pm 3^\circ\text{C}$ and $20 \pm 3^\circ\text{C}$ respectively (D560-57).

(3) Weight loss is used as a measure of freeze-thaw resistance and measured after each cycle (D560-57).

Modification to the existing methods have also been made, as described below:

(1) The test specimens are 5 cm cubes. This decrease in volume is desirable to reduce both material and space requirements for sample preparation and for carrying out the tests, respectively. Moreover, it was originally planned to use unconfined compression strength (UCS) as a measure of freeze-thaw resistance. The standard method for UCS measurements prescribes test specimens of such shape and dimensions.⁵

(2) Measurements of weight loss are carried out on the removed and dried particulate matters, and not on the test specimens. The weight loss is then expressed on a dry basis relative to the original test specimen weight. This approach improves the precision of the weight loss measurements, and more importantly, eliminates the necessity of accounting for moisture changes in the test specimens during the freeze-thaw cycles.

(3) "Control" specimens are used to correct the weight loss measurements. These undergo identical treatment as the test specimens except exposure to a low temperature during the freezing phase. This approach has been adopted to isolate the effect of freezing and thawing from others that might contribute to weight loss, such as matrix dissolution.

(4) The removal of loose particulates is carried out by ultrasonic application followed by rinsing, and not by a wire scratch brush. This approach has been adopted to improve reproducibility and to enhance differences in weight loss, either between control and test specimens or between different test specimens.

A brief description of the procedure is as follows:

- Prepare and weigh test and control specimens (see next section).
- Prepare identical specimen for measurement of moisture content and computation of oven dry weight.
- Each specimen is placed in a covered beaker with known tare weight.
- Beakers containing test specimens are placed in a freezing cabinet, while control specimens are stored in a moist container at room temperature.
- At the end of the freezing phase all of the beakers are filled up with distilled water to cover the specimens and thawed in water.
- At the end of the thawing phase, the specimens are exposed to ultrasonic for 4 minutes, rinsed with distilled water to the beakers of origin and transferred to a new set of beakers. The water containing the removed particulates is evaporated and the dry solids are measured.
- The cycling is repeated 12 times unless specimens lose integrity earlier in the process.

MATERIALS

An aqueous solution containing 0.1 molar of As, Cd, Cr and Pb was used as the waste. Table I is a summary of the types and quantities of the additives used to treat the waste. These have been selected to represent inexpensive s/s processes that are at present widely used,^{6,7} though the composition of the matrix may not reflect the best available s/s technology. For each set of treated waste specimens a corresponding "blank" set (containing no heavy metal) was

also prepared and tested.

Preparation of test specimens, including mixing and molding, was carried out using equipment as specified in the ASTM C305-82⁸ and C192-81.⁹ Modifications to the prescribed procedures were however made, such as lengthening the mixing time to ensure homogeneity. All the test specimens were cured for 28 days at room temperature and in excess of 96% relative humidity.

Table I Summary of Additives Used

Desig.	Additives(b)	Ratio(a)
A	Cement, Fly ash	1:0.45:2.1
B	Lime, Fly ash	1:0.55:1.85
C	Cement, Soluble Silicate	1:0.65:0.60
D	Cement, Bentonite	1:0.55:0.85
E	Gypsum	1:1

(a) Weight ratio, waste:additive: additive, in the order as shown in the second column.

Table II Replicate Weigh Loss measurement results, showing reproducibility of proposed method

Cumulative relative weight loss after indicated freeze-thaw cycle number (% dry basis)(a)

	1	2	3	4	5	6	7	8	9	10	11	12	Av.
TEST SPECIMENS(b)													
Mean(c)	0.59	1.18	2.07	2.73	3.74	4.42	5.29	6.39	7.19	7.98	9.00	10.39	
RSD%	0.74	7.23	13.1	7.37	4.70	8.04	12.2	16.3	13.8	11.5	12.2	7.65	9.5
CONTROL SPECIMENS(b)													
Mean(c)	0.57	1.11	1.66	1.18	2.71	3.22	3.71	4.25	4.78	5.30	5.82	6.34	
RSD%	1.24	1.42	1.84	1.09	0.61	0.85	0.40	0.39	0.17	0.13	0.07	0.20	0.7

(a) Relative to specimen initial weight.

(b) Gypsum process, see Table I;

(c) Arithmetic mean of 4 measurements, specimens prepared from two batches; RSD-ratio of standard deviation to mean in %.

(b) Sources of materials

Cement (Portland Cement Type II) -
Genstar, Edmonton, Alberta
Flyash - Power Plant, Ontario
Soluble silicate (Type N) -
National Silicate, Toronto, Ontario
Bentonite (Voloclay No. 200) -
Western Bentonite, Edmonton, Alberta
Gypsum (Envirostone A, B and C) -
US Gypsum Co., Libertyville, Ill.

RESULTS AND DISCUSSION

Reproducibility

An indication of the reproducibility of the proposed method is shown in Table II, summarizing the weight loss measurement results for both the test and control specimens.

In terms of weight loss measurement, a relative standard deviation of better than 2% could be achieved, as shown by the results for the control specimens. Freezing and thawing, combined with batch-to-batch variation, introduced more scatter, which is not unexpected. A maximum relative standard deviation of 17.0% could be achieved for cumulative weight loss measurements after freeze-thaw cycles.

The results summarized in Table II also show the importance of using control specimens, especially when matrix dissolution is considerable. By this means, the contribution to the total weight loss which is attributed to freezing and thawing could be isolated.

Applicability to Different S/S Processes

Figure 1 shows a comparison amongst the five different

additives listed in Table I. The vertical axis represents cumulative weight loss, relative to the initial weight, expressed on a dry basis and corrected for control specimen weight loss. The horizontal axis shows the number of freeze-thaw cycles.

The results show marked differences in freeze-thaw resistance amongst the systems tested, ranging in cumulative weight loss from 0.1% after 12 freeze-thaw cycles to about 3% after 5 cycles. It is our contention therefore, that the proposed method provides a sensitive means of comparing different s/s processes on the basis of freeze-thaw resistance.

It is also interesting to note the progression of the weight loss. For example, specimen E (Envirostone A) showed very little weight loss up to 8 freeze-thaw cycles, but then there was a dramatic increase in weight loss, followed by formation of cracks. Figure 2 shows an example of a test specimen with cracks.

It should be emphasized that the proposed test method was not developed for extrapolation purposes, to predict freeze-thaw resistance under actual field conditions. No consideration has been given to the various similarity factors that must be accounted for in order to develop predictive capabilities. Nevertheless, the proposed method could provide a rapid indication of the relative freeze-thaw resistance of different s/s processes.

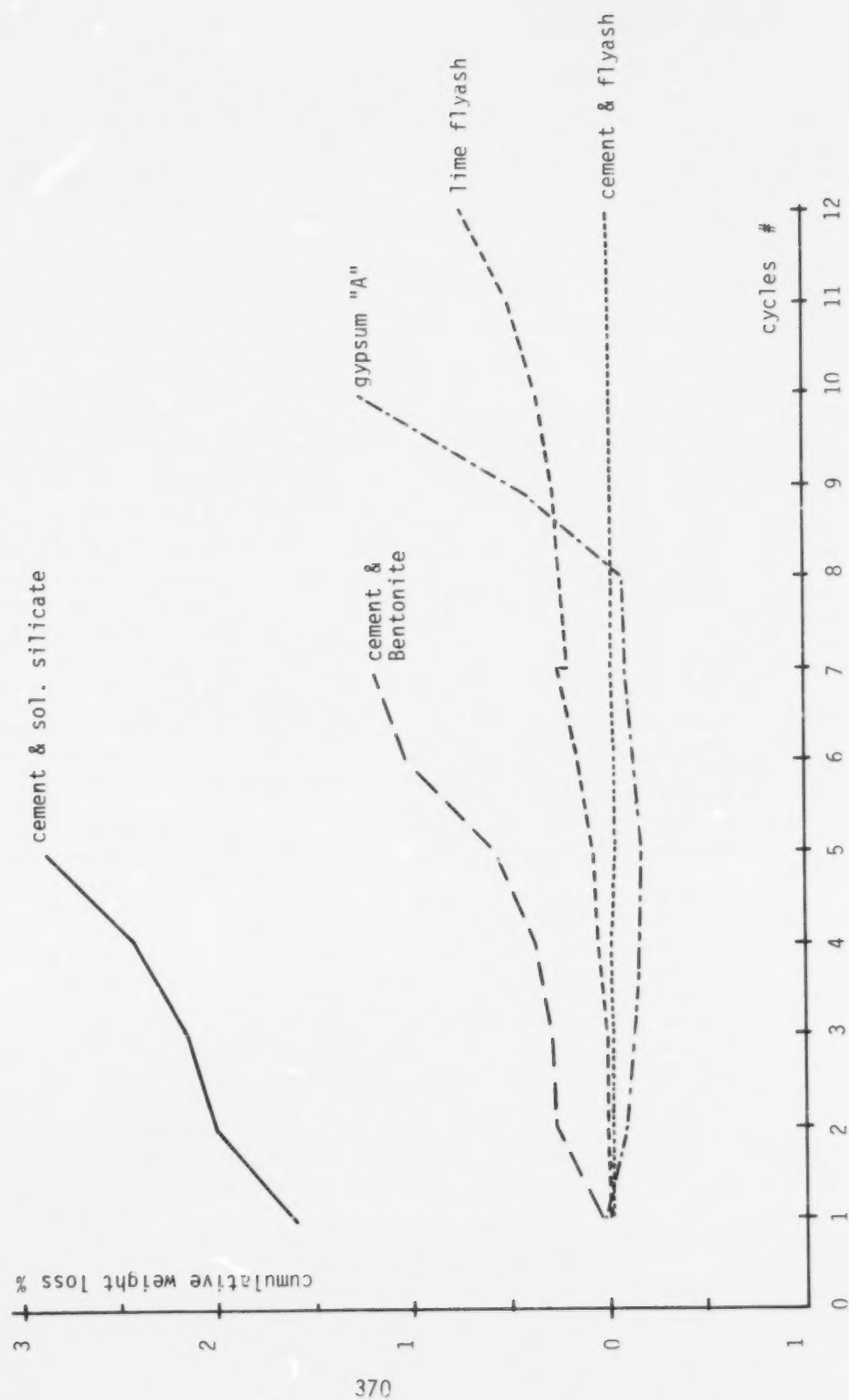


fig. 1

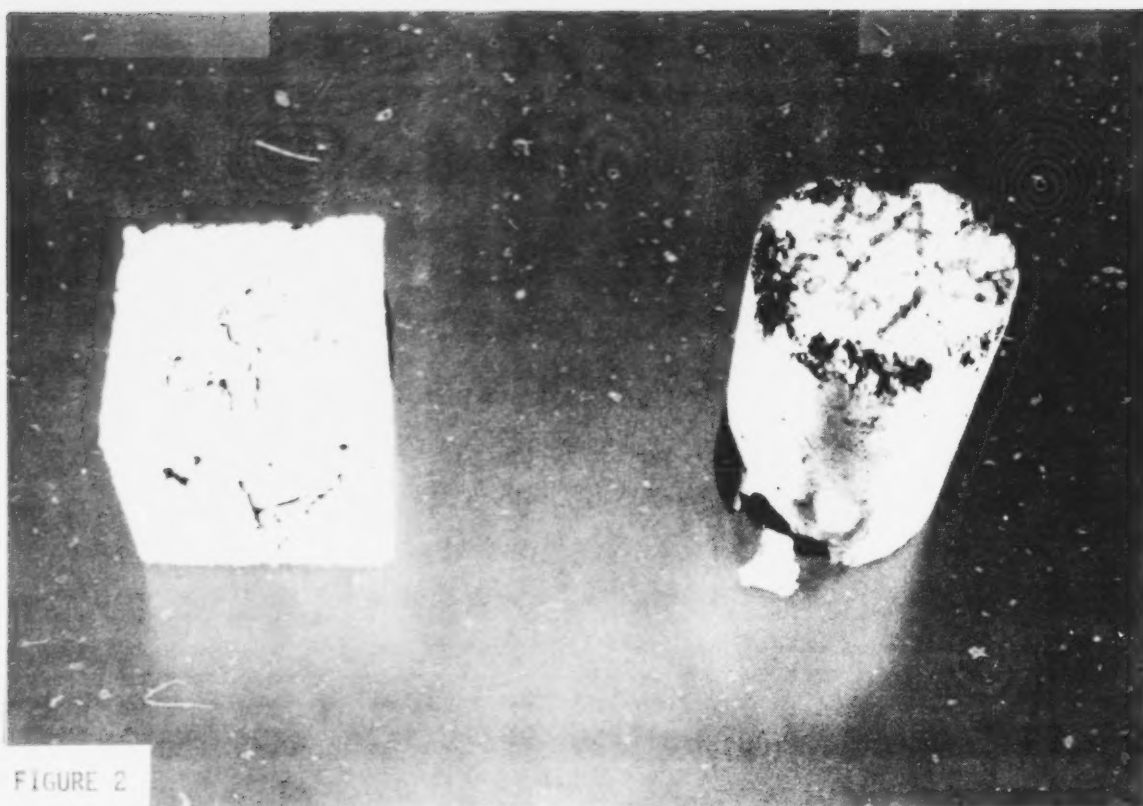


FIGURE 2

Effect of Contaminants

Figure 3 (Matrix C) and 4 (Matrix B) show the differences in weight loss between test and blank specimens that were exposed to freeze-thaw cycles and also those used as control specimens. Also shown in Figure 3 are the number of freeze-thaw cycles at which specimen disintegration occurred.

Somewhat curiously, some of the test specimens which contained contaminants displayed a higher freeze-thaw resistance than the blank specimens in which no contaminant was present. It could be speculated that contaminant-additive interactions or reactions occurred, which resulted in improvements in freeze-thaw resistance. Investigation of the

possible mechanisms is, however, beyond the scope of this paper.

Modifications and Extension of Proposed Method

Ultrasonic Application

A series of tests were carried out to assess whether ultrasonic application was necessary. Elimination of this means of removing loose particulate matters would simplify the method, and moreover, concerns over standardization of the ultrasonic equipment and its method of operation would be eliminated. The results for both test and control specimens are summarized in Table III.

Standard conditions were used by centering samples immersed in

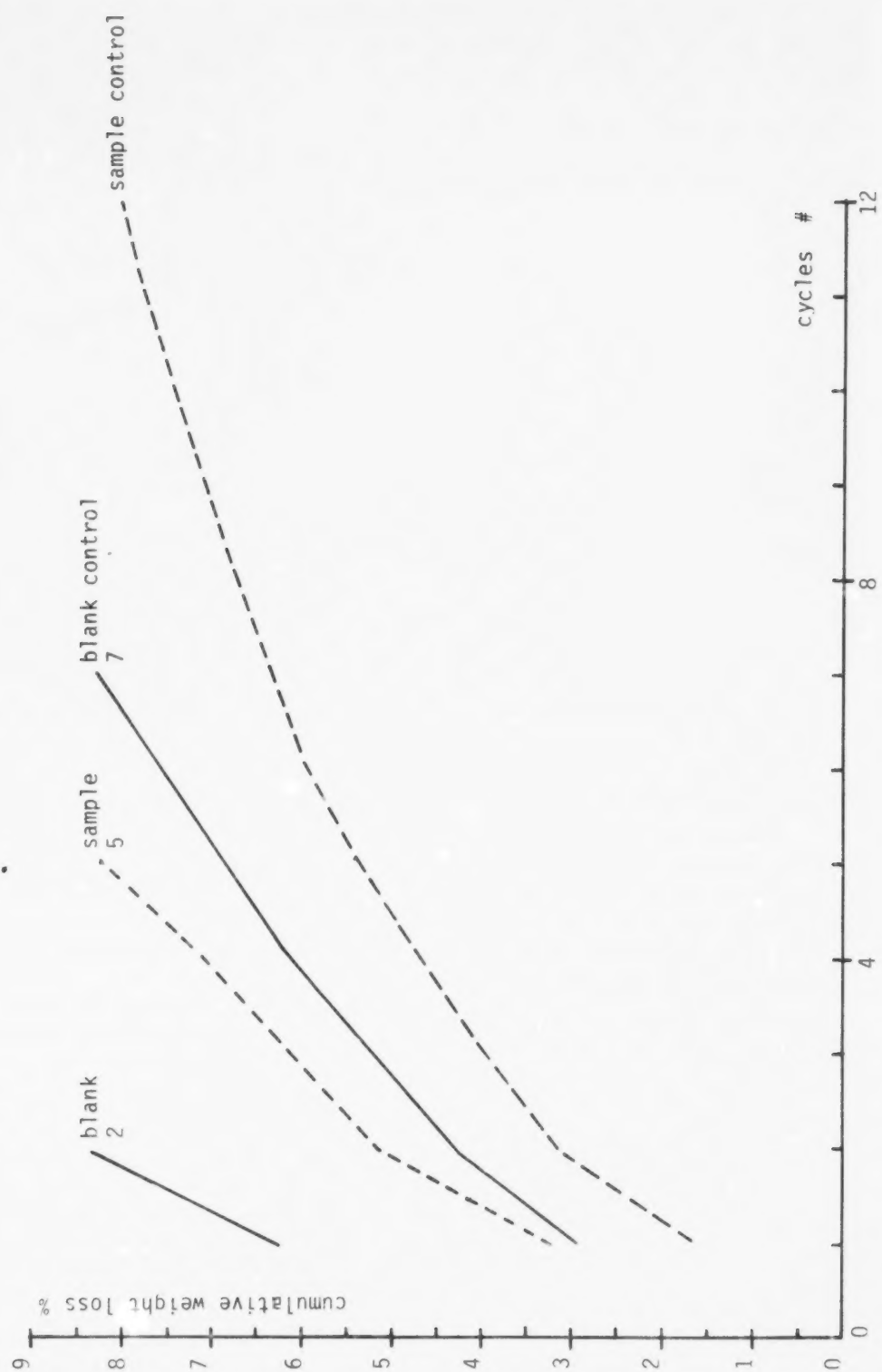


fig. 3

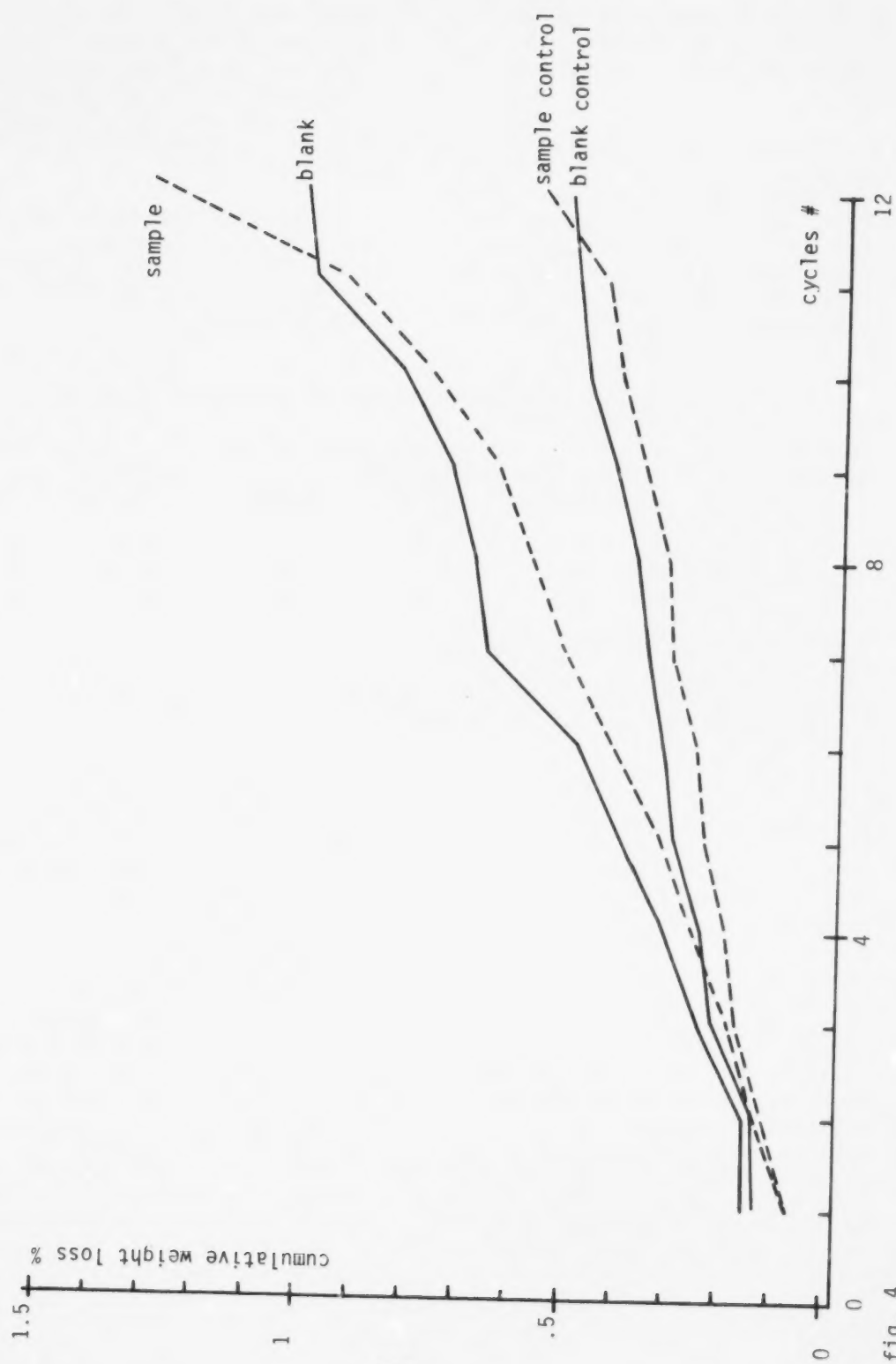


fig. 4

230ml water containing beakers (type Klimax No. 1400) in an ultrasonic bath (type Bransonic 221).

For the control specimens a marginal increase in weight loss was indicated as a result of ultrasonic application. However, for the test specimens no apparent change was observed. In fact, in terms of corrected weight loss (ie. test-control), the effect of

ultrasonic application masked that of freezing and thawing. It would seem that when freezing and thawing alone were sufficient to effect particulate removal, ultrasonic application produced little additional effect.

For the above reason and also for simplicity, ultrasonic application is judged unnecessary and hence will be abandoned in future tests.

Table III Effect of Duration of Ultrasonic Application

Duration (Minutes)	Weight Loss, % (a)					
	Test Specimen (b)			Control		
	Range	Mean (c)	SD (c)	Range	Mean(c)	SD(c)
0	0.55-0.80	0.68	0.08	0.45-0.85	0.61	0.12
4	0.55-0.80	0.70	0.08	0.60-0.80	0.66	0.07
8	0.60-0.80	0.70	0.08	0.65-0.80	0.70	0.05

(a) Relative to initial weight, dry basis

(b) Gypsum system E, see Table I

(c) Computed arithmetic mean and standard deviation (SD) of weight loss measurements over 12 freeze-thaw cycle.

Test Specimen Dimensions

As previously mentioned, 5 cm cubes were used since it was originally planned to incorporate UCS measurements to characterize freeze-thaw resistance. UCS measurements are destructive, hence a large number of specimens need to be prepared. Because of this disadvantage, and furthermore, because weight loss measurements are sufficient to characterize freeze-thaw resistance, in future tests cylindrical specimens, 4.4 cm diameter and 7.4 cm long, will be used. These specimens can be prepared using readily available plastic vials. A

further advantage is thus gained in that these vials are considerably less costly than the metallic molds required to prepare cubical specimens.

Future Plans

A cooperative project, involving US EPA, Environment Canada, the Alberta Environmental Centre and vendors of s/s processes, will be undertaken to assess the applicability of various short-term laboratory test methods.¹⁰ The proposed test method is included in this project. Thus, further information will be gathered on its applicability to a wide variety of wastes, including "real wastes", treated by commercially used s/s

processes. Information on inter-laboratory reproducibility will also be pursued by conducting a round-robin study under of ASTM D-34. Development of the method to an ASTM standard level will then be considered.

Also included in the co-operative project is a test method for measuring wet-dry resistance. The approach used in the proposed method for measuring freeze-thaw resistance will be adopted: the use of weight loss as a measure of wet-dry resistance, control specimens to correct test specimen weight loss measurements, and the same particulate removal method. The wetting and drying phases will be carried out at $20 \pm 3^\circ\text{C}$, $60 \pm 3^\circ\text{C}$ for 24 hrs and 23 hrs, respectively. The weight loss measurements will be carried out after each complete dry-wet cycle.

CONCLUSIONS

The development of a method for measuring the freeze-thaw resistance of solidified/stabilization wastes has been described. Novel features are introduced, including methods for particulate removal and weight loss measurement, and the use of control specimens to isolate the effect of freezing and thawing.

The initial results obtained show promise in terms of reproducibility and ability to detect differences amongst different s/s processes. Various modifications have been introduced to simplify the method, and further tests are planned to assess the applicability of the method to a wide variety of solidified/stabilized wastes and to obtain inter-laboratory reproducibility values.

Adoption of the proposed method for measuring wet-dry resistance will also be assessed.

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PARTITIONING ANALYSIS
OF CHEMICAL SUBSTANCES
AS A TOOL FOR MANAGING HAZARDOUS WASTE STUDIES

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ABSTRACT

Partitioning analysis schemes were applied to determine distribution of representative chemical pollutants within water to air and soil to air pathways. Established theoretical and/or empirical mathematical representations and models; and available chemical property data were used. Information elements for the schemes included the physical, chemical, biological, and environmental characteristics of the chemicals and the partition coefficients. Relative fitting of the parameters into the existing mathematical representations or models was assessed. Certain data inadequacies were taken into account.

The findings suggest that within hazardous waste management studies, partitioning analysis is useful in:

- o Identifying the predominant environmental compartment(s) where a given chemical will reside.
- o Assisting in the design of optimal field sampling programs.
- o Estimating half-life and mobility, degree of bioaccumulation, residence time for degradation and transformation, time of risk exposure, and toxic effects.
- o Establishing bases for the selection of remedial measures.
- o Developing representative conditions for laboratory or pilot-scale treatability studies.
- o Providing guidance for designing study protocols.
- o Assisting engineers in designing remedial disposal methods minimizing adverse environmental impacts.
- o Providing guidance in the formulation of environmental regulations.

INTRODUCTION AND PURPOSE

After a pollutant is released into the environment, it is distributed chiefly among three compartments: air (atmospheric), water (aquatic), and soil (terrestrial). The concentration of a chemical present initially in each compartment is a function of both its properties and type of release. Once present

in the environment, the chemical undergoes dynamic changes which are a function of intercompartmental transfers, transformations, and degradations. If the pollutant is persistent, the potential for eventual uptake by aquatic and terrestrial organisms increases. Consequently through biomagnification, it is

possible for concentrations in biological tissues to reach a level, which may cause significant toxicological hazard to humans and other populations.

Health and environmental hazard or risk assessments can be initiated once the pollutant-favored environmental compartment is delineated. One of the most difficult tasks in performing these risk assessments is adequate screening and testing of large numbers of chemicals under stringent time and budgetary constraints. To alleviate this problem, partitioning analysis can assist in focusing limited resources to key media and elements of the risk assessments.

Water-to-air and soil-to-water partitioning schemes involve the use of mathematical representations or models that are predominantly based on chemical partitioning properties such as the molecular formula, structure, and weight; specific gravity and density; vapor pressure and density; solubility in water and certain organic solvents; octanol/water partition coefficient; soil adsorption coefficient; half-lives related to evaporation, photolysis, hydrolysis, and other physical, chemical, and biochemical reactions. Predictive mathematical models based on the above properties can either be obtained from the available literature or be specifically developed.

APPROACH

The following general categories of the potential transformation and transport pathways were studied.

- o Intercompartmental transfers
- o Transformation, bioaccumulation, and biomagnification
- o Environmental degradations

Each environmental pathway was considered separately as a function of the physical and chemical properties of a given chemical pollutant in relation to the intercompartmental transfer (the transport and redistribution processes among the environmental solid, liquid and gaseous phases.)

Water-to-Air Models

The two models employed in this phase of the study were originally proposed by Dilling (Model I, 1977) and Mackay and Leinonen (Model II, 1975).

Model I

$$H = \frac{16.04 \times P \times M}{T \times S}$$

$$K_1 = \frac{221.1}{(1.042/H + 100) \times M^{0.5}}$$

$$t_{1/2} = (0.6931) \times d / K_1$$

where,

H = Henry's law constant (dimensionless)

P = Vapor pressure (mm Hg)

M = Molecular weight (gm/mole)

T = Absolute temperature ($^{\circ}$ K)

S = Solubility in water (mg/L)

K_1 = Overall liquid exchange constant (cm/min)

$t_{1/2}$ = Evaporation half-life (min)

d = Solution depth (cm)

Model II

$$H = \frac{VP}{WS},$$

$$k_{iL} = \frac{0.2 \times (\text{MW of } \text{CO}_2)^{0.5}}{(\text{MW of Compound})^{0.5}},$$

$$k_{iG} = \frac{30 \times (\text{MW of } \text{H}_2\text{O})^{0.5}}{(\text{MW of Compound})^{0.5}},$$

$$\frac{1}{K_{iL}} = \frac{1}{k_{iL}} + \frac{1}{H \times k_{iG} / (R \times T)},$$

$$t_{1/2} = 0.693 \times L / K_{iL}$$

where,

H = Henry's law constant (atm-m³/mole)

VP = Vapor pressure (atm)

WS = Water solubility (moles/gm)

k_{iL} = Liquid film mass transfer coefficient (m/hr)

k_{iG} = Gas film mass transfer coefficient (m/hr)

K_{iL} = Overall liquid coefficient (m/hr)

MW = Molecular weight (gm/mole)

t_{1/2} = Volatilization half-life (hr)

L = Liquid depth (assumed 1 m)

R = Gas constant = 8.2 x 10⁻⁵ (m³-atm/mole-°K)

T = Absolute temperature (°K)

Water-to-air partitioning was represented by the half-life of a chemical in a water body of given depth. It was assumed that the water depth was 1 m and the water temperature was at 20°C. The partitioning procedures were:

1. Obtain vapor pressure and water solubility data from reliable sources.
2. Calculate Henry's law constant.
3. Apply these values to the Dilling or Mackay and Leinonen models to calculate coefficients/constants and the half-life.

Soil-to-Water Models

The two models adopted for this phase of the study were originally proposed by Kenaga and Goring (Model I, 1980) and Briggs (Model II, 1973).

Model I

$$\text{Log } K_{oc} = 3.64 - 0.55 \times (\text{Log WS}) \pm 1.23$$

order of magnitude
[95% confidence level and correlation coefficient of 0.84]

where,

K_{oc} = Soil/water partition coefficient per unit organic matter (dimensionless)

WS = Water solubility in (mg/L)

Model II

$$\text{Log } Q = (0.524 \times \text{Log } P) + 0.618$$

where,

Q = Soil organic matter/water partition coefficient (dimensionless)

P = Octanol-water partition coefficient (dimensionless)

For the definition of soil adsorption capabilities, we adopted K_{oc} (Kenaga and Goring, 1980) and Q values (Briggs, 1973). We assumed that the soil/water matrix was at an equilibrium temperature of 20°C. The procedures used for calculating K_{oc} and Q were:

1. Obtain water solubility data from reliable sources.
2. Calculate the relevant transfer coefficient(s) in the Kenaga and Goring's and Briggs' models.
3. Calculate K_{oc} and Q values.

Mobility of a given compound from soil to water (e.g., by leaching) is a fun-

ction of soil adsorption coefficients. The mobility rating scheme proposed by Kenaga (1980) is as follows:

- o Immobile ($K_{oc} \geq 1,000$)
- o Moderately to highly mobile ($K_{oc} < 100$)

The mobility rating scheme proposed by Briggs is as follows:

- o Immobile ($Q > 398$)
- o Low ($398 > Q > 74$)
- o Intermediate ($74 > Q > 29$)
- o Mobile ($29 > Q > 4.5$)
- o Very mobile ($Q < 4.5$)

PROBLEMS ENCOUNTERED

The applicability of the proposed partitioning schemes was generally limited by the following:

- o They are less effective for chemical pollutants having inadequate or incomplete data.
- o The analysis was based on purely empirical data and detailed experimental protocols were not established.
- o The schemes were generally applicable to known and pure compounds only.
- o The schemes served as a guide to the partitioning character of the individual compounds studied individually but yielded no information on the environmental partitioning of heterogeneous groups of toxic chemicals.

Furthermore, information was inadequate on the environmental transformation or transport pathways of pollutants for which mathematical models are not readily available. Some of the available models are formulated in terms of kinetic parameters rather than simple physical and chemical data. Application

of these models is limited because they lack published kinetic data for most compounds. Availability of relevant field data are scarce for environmental partitioning scheme development and validation.

RESULTS

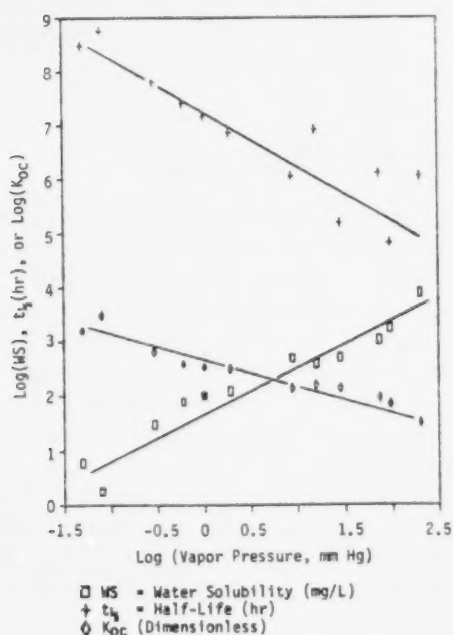
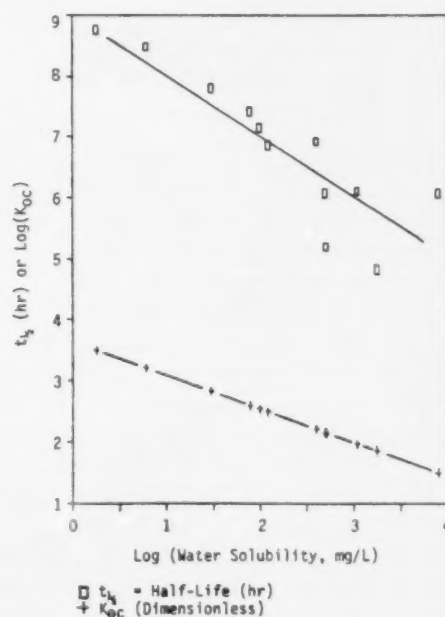
Water-to-Air Partitioning

The results of calculations for the selected compounds are summarized in Table 1. The calculated half-life values range from 4.8 to 14.0 hours for all compounds, except for aniline, isophorone, and phenol having a predicted half-life greater than 382.2 hours. Figures 1, 2, and 3 are plots of the results. The following conclusions can be generalized from Table 1 and these plots:

1. Effects of vapor pressure on water solubility and half-life (Figure 1):
 - o Water solubility increases with increasing vapor pressure
 - o Half-life decreases with increasing vapor pressure
2. Effects of water solubility on half-life (Figure 2):
 - o Half-life decreases with increasing water solubility
3. Effects of molecular weight on vapor pressure, water solubility, and half-life (Figure 3):
 - o Vapor pressure and water solubility decrease with increasing molecular weight
 - o Half-life increases with increasing molecular weight

Table 1. Summary of Water-to-Air Partitioning Analysis

COMPOUND	INPUT PARAMETERS ^a					MODEL I (Dilling, 1977)		MODEL II (Mackay and Leinonen, 1975)			
	VAPOR PRESSURE		MOLECULAR WEIGHT		WATER SOLUBILITY		HENRY'S CONSTANT (dimensionless)	LIQUID		OVERALL	
	(mm Hg)	(atm)	(gm/mole)	(mg/L)	(mole/m ³)			EXCHANGE CONSTANT K_L (cm/min)	HALF- LIFE (hr)	HENRY'S CONSTANT (atm·m ³ /mole)	TRANSFER COEFF. K_{TL} (m/hr)
BENZENE	95.20 ^a	1.25E-01	78.11	1.78E+03 ^a	22.79	2.29E-01	0.259	4.8	5.50E-03	0.144	4.8
TOLUENE	28.40 ^a	3.74E-02	92.13	5.15E+02 ^a	5.59	2.78E-01	0.222	5.2	6.68E-03	0.133	5.2
CHLOROFORM	200.00 ^b	2.63E-01	119.39	7.95E+03 ^b	66.59	1.64E-01	0.190	6.1	3.95E-03	0.114	6.1
MONOCHLOROBENZENE	8.80 ^c	1.16E-02	112.56	5.00E+02 ^c	4.44	1.08E-01	0.190	6.1	2.61E-03	0.114	6.1
TRICHLOROETHYLENE	74.00 ^d	9.74E-02	131.39	1.10E+03 ^d	8.37	4.84E-01	0.189	6.1	1.16E-02	0.113	6.1
1,3-DICHLOROBENZENE	1.89 ^e	2.49E-03	147.01	1.23E+02 ^e	0.84	1.24E-01	0.168	6.9	2.97E-03	0.101	6.9
TETRACHLOROETHYLENE	15.80 ^f	2.08E-02	165.82	4.00E+02 ^f	2.41	3.58E-01	0.167	6.9	8.62E-03	0.100	6.9
1,2-DICHLOROBENZENE	1.00 ^g	1.32E-03	147.01	1.00E+02 ^g	0.68	8.05E-02	0.161	7.2	1.93E-03	0.097	7.2
1,4-DICHLOROBENZENE	0.60 ^g	7.89E-04	147.01	7.90E+01 ^g	0.54	6.11E-02	0.156	7.4	1.47E-03	0.093	7.4
1,2,4-TRICHLOROBENZENE	0.29 ^g	3.82E-04	181.45	5.00E+01 ^g	0.17	9.60E-02	0.148	7.8	2.31E-03	0.089	7.8
1,2,4,5-TETRACHLOROBENZENE	0.05 ^g	6.58E-05	215.90	6.00E+00 ^g	0.03	9.84E-02	0.136	8.5	2.37E-03	0.082	8.5
HEXACHLOROCYCLOPENTADIENE	0.08 ^h	1.05E-04	272.77	1.80E+00 ^h	0.01	6.64E-01	0.132	8.8	1.60E-02	0.079	8.8
ANILINE	1.00 ⁱ	1.32E-03	93.13	3.66E+04 ⁱ	393.00	1.59E-04	0.003	382.2	3.55E-06	0.002	382.3
ISOPHORONE	0.20 ^j	2.63E-04	138.21	1.20E+04 ^j	86.82	1.26E-04	0.002	513.7	3.03E-06	0.001	513.8
PHENOL	1.00 ^k	1.32E-03	94.11	8.20E+04 ^k	871.32	6.28E-05	0.001	845.7	1.51E-06	0.001	845.9

^a Data are based on a temperature at or nearest to 20°C.^b Mackay and Leinonen (1975); ^c Dilling, et al. (1975); ^d Varshauer (1977); ^e Richardson (1968); ^f Kanaga and Goring (1980); ^g Irish (1963); ^h Callahan (1979); ⁱ Sax (1979); ^j Hawley (1977); ^k Kanaga (1980); and ^l Browning (1965).Figure 1. Effects of Vapor Pressure (VP) on Water Solubility, Half-Life, and K_{oc} Figure 2. Effects of Water Solubility on Half-Life and K_{oc}

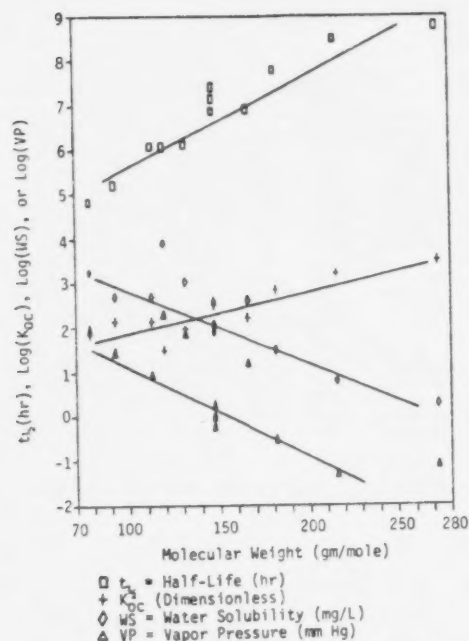


Figure 3. Effects of Molecular Weight on Half-Life ($t_{1/2}$), K_{oc} , Water Solubility and Vapor Pressure

These findings are most pronounced for the chlorinated benzenes, probably due to their similarity in molecular structure. Extrapolating this finding, partitioning analysis may be useful in predicting the volatilization potential of exotic compounds of unknown physical properties by drawing analogies from closely similar compounds within the same family. An increase in chlorine atoms per molecule causes an increase in molecular weight, a decrease in vapor pressure, a decrease in water solubility, and an increase in half-life. Compounds of higher molecular weight and longer half-life tend to favor the aquatic over the atmospheric compartment. Other observations, awaiting further confirmation, are that the structural positions of chlorine atoms on the benzene rings somehow dictate the values of

vapor pressure and water solubility, and hence the half-life of the compound within the chlorinated benzene family.

Aniline, isophorone, and phenol have vapor pressure values very close to that of most compounds listed in Table 1, but they also have high water solubilities. The latter property hinders the volatilization process.

Focusing on the volatilization potential or half-life of various benzene derivatives, some guidance information relevant to hazardous waste management can be preliminarily deduced. For example, high volatile substances, which upon their release to the environment favor air pathways, are more amenable to removal by air or steam stripping. Furthermore, half-life data can be used to estimate the emission strength of sources and to assess their risk potential within hazardous waste sites or production facilities.

Soil-to-Water Partitioning

The results of the calculations of the soil adsorption capabilities for the compounds studied are summarized in Table 2. The calculated K_{oc} values range from 9 to 3,159. The calculated Q values range from 5 to 1,162. In general, K_{oc} and Q values and their respective mobility ratings agree with each other very well. Figures 1, 2, and 3 contain plots of results for all compounds except for aniline, isophorone, and phenol. The following conclusions can be generalized from Table 2 and these figures:

1. K_{oc} decreases with increasing water solubility and vapor pressure (Figures 1 and 2, respectively)

Table 2. Summary of Soil-to-Air Partitioning Analysis

COMPOUND	MODEL I (Kenaga and Goring, 1980)			MODEL II (Briggs, 1973)		
	SOIL ADSORPTION COEFFICIENT		RELATIVE MOBILITY*	OCTANOL-WATER PARTITION COEFFICIENT		RELATIVE MOBILITY***
	WATER SOLUBILITY (mg/L)	K_{oc} (dimensionless)		Log P (dimensionless)	Q (dimensionless)	
PHENOL	8.20E+04 ^a	9	Highly mobile	0.23**	5	Mobile
ACRYLONITRILE	7.50E+04 ^b	9	Highly mobile	0.26**	6	Mobile
ANILINE	3.66E+04 ^a	13	Highly mobile	0.51**	8	Mobile
ISOPHORONE	1.20E+04 ^c	25	Highly mobile	2.26**	63	Intermediate
CHLOROFORM	7.95E+03 ^d	31	Highly mobile	1.90**	41	Intermediate
BENZENE	1.78E+03 ^e	71	Moderately mobile	2.13**	54	Intermediate
TRICHLOROETHYLENE	1.10E+03 ^d	93	Moderately mobile	1.72**	33	Intermediate
TOLUENE	5.15E+02 ^f	141	Moderately mobile	2.21**	60	Intermediate
MONOCHLOROBENZENE	5.00E+02 ^g	143	Moderately mobile	2.18#	58	Intermediate
TETRACHLOROETHYLENE	4.00E+02 ^d	162	Moderately mobile	2.08**	51	Intermediate
1,3-DICHLOROBENZENE	1.23E+02 ^h	309	Moderately mobile	3.44#	263	Low
1,2-DICHLOROBENZENE	1.00E+02 ⁱ	347	Moderately mobile	3.40#	251	Low
1,4-DICHLOROBENZENE	7.90E+01 ^j	395	Moderately mobile	3.39#	248	Low
1,2,4-TRICHLOROBENZENE	3.00E+01 ^k	672	Immobile	4.17#	635	Immobile
1,2,4,5-TETRACHLOROBENZENE	6.00E+00 ^l	1,629	Immobile	4.67#	1,162	Immobile
HEXACHLOROCYCLOPENTADIENE	1.80E+00 ^g	3,159	Immobile	3.99#	511	Immobile

* Based on the mobility rating method proposed by Kenaga, 1980.

** Calculated using the equation suggested by Kenaga and Goring, 1980.

Values reported by Hensch and Leo, 1979.

*** Based on the mobility rating method proposed by Briggs, 1973.

^aKenaga and Goring (1980); ^bKenaga (1980); ^cBrowning (1965); ^dDilling et al. (1975); ^eMackay and Leinonen (1975);^fVerschuere (1977); and ^gCallahan (1979).2. K_{oc} increases with increasing molecular weight (Figure 3)

These general findings are also most consistent for the family of chlorinated benzenes, probably due to their similarity in molecular structure. Extrapolating this finding, partitioning analysis may be useful in predicting the mobility of exotic compounds of unknown physical properties by drawing analogies from closely similar compounds within the same family. An increase in chlorine atoms per molecule causes a decrease in water solubility (which correlates well with an increase in molecular weight), an increase in K_{oc} or Q , and a decrease in mobility from aquatic to terrestrial compartments. Compounds of higher K_{oc} or Q tend to resist leaching and stay in the terrestrial compartment.

Other tentative observations, awaiting further confirmation, are that the structural positions of chlorine atoms on the benzene rings somehow dictate the values of water solubility, and, hence, the mobility of the compound within the chlorinated benzene family.

Regarding guidance information for the management of hazardous waste, preliminary findings suggest that compounds having high mobility tend to escape from their sources of release by leaching and to contaminate surface water and groundwater systems. These compounds are more effectively recovered from water media (e.g., via groundwater pumping or leachate interception) for central onsite or offsite treatment.

Compounds having low mobility tend to remain at the source, potentially causing bioaccumulation and biomagnification problems. However, these compounds can be effectively removed by excavation or controlled by source containment and encapsulation.

ACKNOWLEDGEMENTS

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This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

RECYCLING AND CLEANER TECHNOLOGY
AS A MEANS OF HAZARDOUS WASTE MANAGEMENT

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ABSTRACT

Increasing amounts of wastes, new hazards, new types of wastes, and limited possibilities for disposal or incineration of hazardous wastes create the need for new ways in hazardous waste management.

Great progress has been made in the development of new technologies for treating hazardous wastes, but the so-called "end-point-solutions" will not be sufficient to solve the problem.

Recycling and cleaner technologies are presented as new concepts and means for hazardous waste management.

Recovery methods as a part of recycling activities have great importance and are demonstrated by some examples.

Cleaner technologies try to avoid hazardous waste problems by regarding the whole production and product-life cycle. Problems and examples of the diffusion of cleaner technologies are discussed.

Denmark has established a system for promoting recycling and cleaner technologies activities; some experiences are presented.

INTRODUCTION

accept new industrial installations at various distances from the homes. Source: /U.S. Council.../)

Hazardous wastes are the new challenge of our time--all over the world. We are all aware of increasing amounts of wastes; household wastes, post-consumer wastes, industrial wastes, agricultural wastes and--last, but not least--hazardous wastes. This is a threat to all nations in that, not only are the amounts of wastes increasing, but also the dangerousness and the risk, especially of hazardous wastes. People feel this and, as an example of their opinion and their feelings, I will show a result of a national opinion survey which demonstrates the need for active work to find new ways of dealing with hazardous wastes. (See Figure 1: Cumulative percentage of people willing to

Figure 1 shows the lowest percentage of people willing to accept new disposal sites for hazardous waste chemicals in their neighborhood--even nuclear power plants are not as threatening as those disposal sites! It is, furthermore, becoming more and more difficult--at least in Europe--to find suitable and accepted disposal sites for all kinds of wastes. We are confronted with increasing amounts of hazardous wastes and we need new solutions for hazardous waste management!

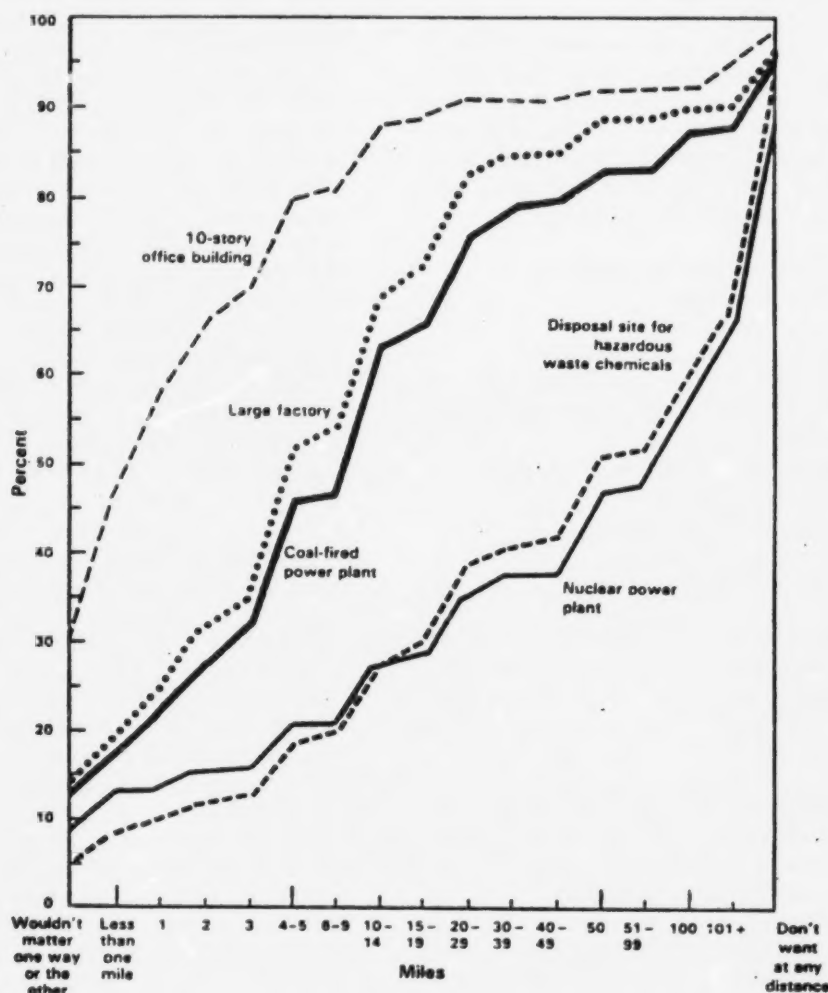
In the future we will have to deal with new production methods, with new products, and with new environmental problems: this strengthens the need not only for new technologies, but even more for new strategies and concepts for

treating hazardous wastes--and recycling and cleaner technologies are the approaches for solving these problems in the future!

Figure 1. Cumulative percentage of people willing to accept new industrial installations at various distances from their homes.

Hazardous Waste Treatment

Hazardous waste is a very wide and unprecise term--it covers generally all wastes which are regarded as toxic, reactive, corrosive or radioactive. Just the fact that you can find two such divergent numbers as 150 million tons versus 67 million tons, as the amount of



U.S. Council on Environmental Quality, Department of Agriculture, Department of Energy, and Environmental Protection Agency: Public Opinion on Environmental Issues: Results of a National Public Opinion Survey, Washington, Government Printing Office, 1980.

hazardous waste production projected for the United States in 1985, shows the problem of defining and of controlling hazardous wastes!

I do not want to add a new definition to the existing ones; I just take hazardous wastes as a problem which

has to be solved! In the past it was easy to dump those wastes, but an increasing understanding of our environment, a rise in public consciousness, and more complete environmental legislation supported the development of physical, biological and chemical treatment methods for hazardous wastes. There is still a need, and this will always exist, to find new ways because the most predominant present methods of hazardous waste treatment (listed below), as, for example, they are used in the United States, will be neither sufficient nor allowed in a couple of years, or they will become too costly:

- indiscriminate dumping
- drum dumping
- ocean dumping
- pooling for evaporation
- encapsulation and fixation
- placement into lined disposal sites
- spraying into the ground
- mixing with soil
- deep well injection
- ocean burning
- incineration

Emphasis is currently placed on developing "new" advanced methods, still dealing with the three so-called "end-point"-solutions, which are as follows:

- a) Destruction of the hazard or the hazardous waste. This is achieved either by biological degradation methods or by thermal processes such as high temperature fluid wall (HTFW)-, fluid bed-, or molten salt-incineration; pyrolytic processes; plasma arc reactions; microwave plasma technologies; wet air oxidation (WAO); or supercritical fluid (SCF) oxidation; among other destruction technologies.
- b) Reduction of the hazard or the hazardous waste. There is much

work done in developing new chemical or biological methods. The most outstanding results seem to be found in the field of enzyme technologies and genetic engineering ('gene splicing') for development of new microbial strains which are capable of degrading previously recalcitrant organic chemicals; but progress has also been achieved in development of chemical processes that reduce the hazard and danger of heavy metal wastes (as, for example, the conversion of hexavalent-chromium waste to the trivalent state) or that involve the oxidation or hydrolization of organic compounds. Other examples could be the use of reduction agents, different chemical treatments, photolysis, and gamma irradiation methods. But physical processes can also be used to reduce the hazard--let us just take as examples distillation, absorption, and extraction by supercritical fluids; as well as different membrane processes such as ultrafiltration, reverse osmosis, dialysis and electrodialysis, and freezing and crystallization processes.

- c) Isolation of hazardous wastes. Progress has also been achieved in the isolation of hazardous wastes, which has to be regarded as the most traditional and conventional of end-point treatment methods. There have been achieved better knowledge and safer methods of disposing wastes, either in secure landfills or by neutralizing, solidifying, or encapsulating the wastes in cement or pozzulano-based materials, thermo-plastic materials, organic-polymers, or glassification materials; but there is still a great deal of uncertainty about the long-term effects of these methods.

But even in achieving these end-points there will, in almost all cases, remain the need for disposal or isolation of residuals, and there will always be an emission of stack gases and

effluents, because none of the treatment methods can obtain a zero level of pollution.

Recycling and Cleaner Technologies as Farsighted Means of Hazardous Waste Management

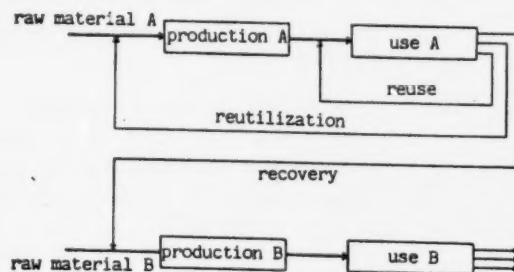
Many of the above named new methods for the treatment of hazardous wastes are the result of the development or adaption of new industrial production methods or reactor designs, as in the case of fluid bed reactors. By economically and technologically improving production methods, technologies, and systems, people became more and more aware of minimizing production spills and wastes--and one of the means to achieve this was recycling.

Recycling

Recycling has for a long time been an integral part of resource management, adding to materials supply and alleviating resource depletion. But in the recent years recycling has had an important role as a means in waste management, and there are good chances for establishing recycling as a means of hazardous waste management--though there are still a lot of barriers and constraints.

But what is recycling? Well knowing that there are a lot of diverging definitions, I will explain, by the next figures, which possibilities there are to use materials physically again, to recycle them.

Figure 2. Recycling Possibilities.
Source: Muller



We all know the principle of reusing a product for its original purpose, such as a returnable bottle, or a material for its original purpose (glass from broken bottles), and we also know a lot of other materials which are used in such recycling processes. Scrap, rubber, plastics, paper and glass are examples for these well-known processes--but we all know as well that much more could be done in these traditional fields of recycling activities!

But recycling has also become an important part of hazardous waste management activities--either for directly regaining economic value or by combining environmental needs with recovery activities. Recycling of waste oils, asphalts, solvents and acids are well known, but not fairly well used examples for recycling activities in the field of hazardous wastes.

It is obvious that the possibilities for a direct recycling of hazardous wastes, both technologically and economically, seem to be rather limited because of the increasing complexity of many production processes and production wastes. But there are still a lot of often surprising possibilities--for example the recycling of petrol from the petrol-laden air which is emitted under each tankfilling operation.

Recycling as a means of hazardous waste management has become of greater

importance for those activities which have been called "recovery". Let us just look at some examples which show that there are a lot of possibilities which can be used in an economic way:

- In the electronics industry you can find a lot of copper containing wastes from excess copper which is removed by means of hydrochloric acid. This waste liquid could go to special hazardous waste treatment plants to end up as filter cakes which have to be deposited in controlled landfills. But on the other side is copper, a micro-nutrient in fertilizers, where the Cu-requirement is approximately 01%--and therefore some fertilizer producers are recycling the copper from copper-containing wastes from the electronics industry.
- Another example could be the recirculation of process waters from the production of glass wool. These waters contain hazardous organic compounds and are now recirculated for the production of a binding agent which is used for the production of glass wool.
- Acid wastes from sulphate based titan-dioxide production can be recycled in an energy saving manner. Thus it can be achieved that no acid wastes have to be dumped in the ocean.
- Bottom products from the distillation of solvents containing wastes from the paint and colour industry can be recirculated as fillers in certain paint types.
- Pickling acid wastes and electrolytic pickling baths from the aluminum industry are hazardous wastes which can be recovered and converted by

special combinations of these two waste streams, whereby sodium aluminate (NaAlO_2), aluminum sulphate- $\text{Al}_2(\text{SO}_4)_3$ - and Glauber's salt (mirabilite, $\text{NaSO}_4 \cdot 10 \text{H}_2\text{SO}_4$) can be produced.

There are a lot of other examples for the recycling of materials by the recovery of hazardous wastes--but it must be said that there is still a need for further development.

Cleaner Technologies

The development of extended recycling and recovery processes was the first step on the way to a new concept in managing waste problems--cleaner technologies, known also as low-waste-technologies.

Though there are many differences in defining this term, cleaner technologies should be regarded as those production measurements which reduce the quantity and the hazard of all types of emissions of a production cycle, which can be illustrated by the following figure:

It is obvious that a recycling policy just covers those production or product wastes which have occurred, while cleaner technologies try to avoid the origin of wastes and emissions, as far as possible, by regarding the whole production and product cycle.

How can this be achieved?

There are three principle ways of reducing the level of emissions and wastes:

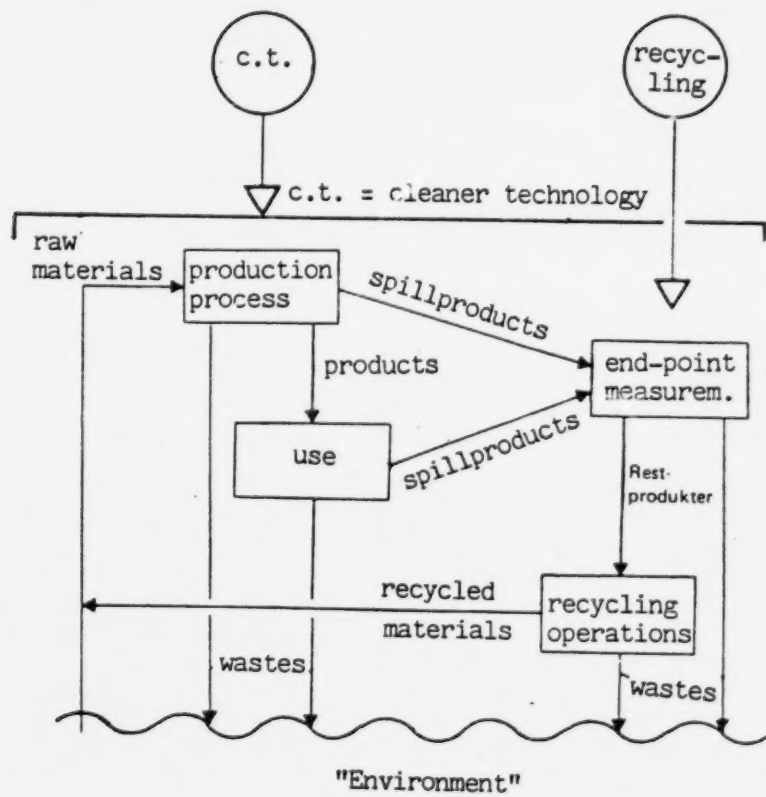
Figure 3: Cleaner Technologies and the Production Cycle.

Source: Miljostyrelsen

- a) Choice of other or alternative raw materials
- b) Development of new processes
- c) New or alternative product design

ad a: It is a basic principle that those raw materials which contain fewer

Figure 3



pollutants result in fewer environmental emissions; but also the choice of alternative materials with the same function in the production process will make a given technology cleaner. These substitution processes can be divided into physical (such as replacement of transformer oils by PCB-free oils), quantitative (such as using thinner coatings) or functional (as in replacement of solvents in paints by water) substitutions.

ad b: The development of new processes is a very important part of a cleaner technology conceptualization, and there are numerous examples of cleaner technologies avoiding airborne, liquid or solid hazardous wastes:

- Development of a non-polluting process for recovering 99.99%-pure lead from discarded batteries. The method reduces lead and sulphur dioxide emissions by avoiding smelting, the conventional way of recovering lead from spent batteries. The new process uses electrolytic melting and subsequent chemical/electrolytical operations.
- Development of an (as yet unpublished) ion-exchange process, which converts waste gypsum (CaSO_4) and cheap potassium chloride into the valuable fertilizer component potassium sulphate (K_2SO_4) and harmless calcium chloride (CaCl_2). This process gives a profit compared to the conventional production and, at the same time, gypsum waste is avoided and the heavy metals from the preceding rock-phosphate treatment process--especially copper, lead, zinc, cadmium and mercury--can be precipitated.

- Development of alternative spray-coating processes or production technologies for fly-ashes or different filter dusts in order to minimize solid hazardous wastes.

ad c: New or alternative product design includes substitution of function, materials, and construction. These substitution methods are important in hazardous waste management, as the following examples show:

- substitution for mercury-containing batteries of zinc-oxygen batteries to avoid mercury emissions from refuse incinerators
- development of water-based and solvent-free paints and colours
- development of chlorine-free bleaching processes in the pulp and paper industry
- replacement of cadmium in colouring pigments
- substitution for PCB-containing oils
- substitution for halogenated hydrocarbons as propellant, sponging or foaming agent
- development of new construction principles and materials

It is apparent that the conceptualization of cleaner technologies is very complex, and that the development of new raw materials, production processes or products will take time, as the following table shows.

Figure 4: Levels of Substitution and Associated Development Times.

Source: Schlabach

Level	Development time (yr)
1 Noninteractive material substitutions Assembly or component change	1 - 3
2 Development of new material or chemical process	3 - 4
3 Interactive materials substitution Electronic technology change Subsystem or small system development	4 - 5
4 Systems of reasonable complexity	~7
5 Complex weapon systems	~10
6 Telephone exchange technology	~13
7 Time for scientific discoveries to find large-scale technical application	~15

Many will claim that all new developments concerning products, production processes, and emission equipment can be regarded as cleaner technologies because of their effect on reducing emissions and spill products, and as a consequence of minimizing production costs--but isn't that too easy to ease our consciences?

Cleaner technologies should be regarded as those technologies which are a real and intended alternative to existing technologies, from an environmental point of view; the environmental benefits should not be regarded as an accidental by-product!

Recycling and Cleaner Technology in Denmark

Denmark has passed a new law on recycling and cleaner technology which enables the state, to support all types of recycling activities concerning materials. On the other hand, it is possible to promote cleaner technology by financing or supporting research and information activities or research and demonstration projects.

It would be inappropriate to try to explain and discuss this law here. Some experiences with this

law, which was passed in the extended form including cleaner technologies by October 1, 1984, can be given:

- a) We feel that recycling activities have been promoted very much by this law, and that information activities are of great importance to the attitude of the population and the result of the recycling activities.
- b) The importance of easy, consumer-oriented collection systems is evident both for households and industries. This is a very important factor for separation and recycling activities concerning hazardous wastes.
- c) It takes time to develop and introduce cleaner technologies in the industry, especially in small and medium sized enterprises.
- d) There is a great interest in participating in our recycling-and cleaner technology program, and we feel that we are promoting this concept a lot. We hope to be able to extend our activities more towards hazardous wastes.
- e) A great incentive, or press, for the promotion of cleaner technologies is given by environmental law activities--and it always turned out that cleaner technologies are paying for themselves.

SUMMARY AND CONCLUSIONS

1. Increasing amounts of wastes, increasing hazards, and new technological developments make solving future problems by new way of managing hazardous wastes inevitable.
2. Conventional ways of treatment will become more and more insufficient both economically and environmentally.
3. Recycling is becoming an integrated part of the industry's activities,

but there are still a lot of unsolved problems.

4. Cleaner technologies offer new and non-traditional possibilities for solving hazardous waste problems by regarding the complete product life cycle.
5. It seems that all recycling and cleaner technology activities can be ensured by law and financial support measurements by state authorities.

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DEWATERING OF HAZARDOUS WASTES USING REVERSIBLE GEL ABSORPTION

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ABSTRACT

We have studied the technical feasibility of using gels to concentrate aqueous waste streams. Potential applications focus on extracting pure water from wastewaters that contain low concentrations of hazardous solutes in order to reduce volumes and concentrate the hazardous material. It has been demonstrated that water sensitive cross-linked gels absorb water while excluding macromolecules that are larger than the gel pore size. Exclusion of ionic solutes can be obtained using gels that contain potentially ionizable groups such as the cross-linked, partially hydrolyzed polyacrylamide gels. Gels have been contacted with solutions containing a wide range of different molecular weight-size solutes. The gels expand by imbibing water. The expanded gel is separated from the concentrated raffinate by draining (filtration) and regenerated. Gel volume is sensitive to pH. It collapses when acidified, yielding an extract of water. A cyclic process of swelling, acidification to release water, and gel reuse has been demonstrated. The process is similar to solvent extraction with the added feature that it separates by molecular size.

INTRODUCTION

Innovative methods for managing aqueous hazardous wastes are needed. Presently available methods of treatment are costly, particularly when the pollutants are dispersed at low concentrations in large volumes of water. The concept of concentrating the waste stream by removing water is attractive because it facilitates subsequent reuse, disposal or destruction of the waste material. The alternative of extracting the pollutant from the water phase can involve high costs because of the

need for essentially complete capture of hazardous materials. Research was therefore initiated to assess the feasibility of removing water using water sensitive cross-linked gels that can be easily regenerated.

APPROACH

Polymeric materials possessing the ability to swell in water without dissolving have been described in the literature (1,20). Swelling is a consequence of the affinity of the chemical structure of the gel for

water. Swelling is also affected by the degree of cross-linkages and the potential for ionization. Cussler *et al.* (3) suggested that appropriately cross-linked, partially hydrolyzed polyacrylamide gels could serve as selective extraction agents because these gels have unusual swelling characteristics. Such gels absorb water (a low molecular weight solvent) but reject high molecular weight solutes that are larger than the average pore diameter of the hydrogel. The gels can be regenerated by imposing a small change in process conditions such as pH (11), temperature (17,18), electric field (26), solvent composition (17, 18,24), or salt concentration (7). These changes cause the gels to collapse, thereby releasing much of the water phase.

It has been shown that dramatic changes in volume occur as a result of small changes in process conditions when some of the side groups of the gel network undergo ionization. Ionization sets up localized negative charges. Small numbers of charge sites, around 1% (15), are effective. The resultant ionic matrix therefore expands and imbibes water while excluding macromolecules by steric exclusion and ions by Donnan exclusion.

The manner in which the gels are used in an extraction process is shown in Figure (1). Gel material is added to the wastewater solution. The gel swells by absorbing water but excluding high molecular weight solutes. The raffinate solute concentration increases accordingly. It can be separated from the swollen gel by draining or filtration. The swollen gel is now regenerated by adding acid. Since the gel volume is very sensitive to pH change, it col-

lapses and releases the absorbed water. The collapsed gel is again drained, filtered to remove water. Finally, the acidified gel is neutralized with a small amount of base, enabling it to swell again when added to another batch of solution.

The first part of this process, concentrating macromolecular solutions by allowing gels to swell in them was first reported by Flodin *et al.* (8). Specific applications have developed sporadically since then (1,4,7). Despite its success in concentrating solutions, the technique was limited in application due to the lack of an efficient method for regenerating the gel (drying was the only means). The second part of this process, the drastic swelling and collapse behavior of the gels in solvent, has been studied primarily as a type of phase transition behavior (5, 15,25). Interest in this area was accelerated by Tanaka's 1978 (18) report of a discrete change in gel volume with an infinitesimal change in solvent composition.

THEORY

The proposed separation process relies on regenerating the gel by changing its volume via decreasing the pH. This variation of gel volume with pH can be estimated using a modification of Flory-Huggins theory for polymer solutions (6,11,12,15,16). Theoretical models that describe volume changes in ionic nature of the gel have been described by several investigators (9,13,15,25). Of these, the model developed by Cussler *et al.* (3), is the simplest.

$$(1) \quad V^{-2/3} \propto \frac{R + K^{-1}}{B}$$

where

V = volume of gel

R = concentration of potentially ionizable groups
 $[R\ COO\ H] + [R\ COO^-]$

K = ionization constant

$K = [R\ COO^-]/[R\ COO\ H][OH^-]$

B = total base added to an acid gel

Equation 1 shows that gel volume to the $-2/3$ power should vary linearly with the reciprocal of the amount of base added.

EXPERIMENTAL PROCEDURES

The gel used in initial experiments was made by hydrolyzing cross-linked polyacrylamide beads produced commercially as packing for gel permeation chromatography (BioRad Laboratories, Richmond, CA). It is sold as Bio-Gel P-6 and has a particle size in water of 150-300 μ m. The gel was hydrolyzed for 24 hours at 323°K in 0.50 M Na_2CO_3 (19). Later work has focused on polyacrylamide gel produced in our laboratory. Details of preparation will be presented at the conference.

Model solutes included a variety of chemicals. Sugar, urea, and sodium chloride were reagent grade (Fisher) and were used as received. Polystyrene latex particles 910 nm in diameter were purchased commercially (Duke Scientific, Palo Alto, CA). Polystyrene latex particles 34.6 nm in diameter were a gift of Dr. Hamish Small (Dow Chemical Co., Midland, MI). Colloidal silica particles (Nalco Chemical, Chicago, IL) were 5 nm in diameter. Bovine serum albumin (Sigma Chemical, St. Louis, MO) was dialysed and then recrystallized.

Hemoglobin was a highly purified sample obtained from Dr. Rufus Lumry (University of Minnesota). The sample of polyethylene glycol used (J.T. Baker, Phillipsburg, NJ) is sold as having 68-84 monomer units and a molecular weight of 3000-37000 daltons.

Starting in late 1984, a series of tests using potentially hazardous chemicals were initiated. They include pentachlorophenol, heavy metals, and their organic complexes. While the results of this work were not available at the time of writing, they will be reported at the conference.

Experiments were carried out by contacting 0.5 g of dry gel with 20 g of solution. The materials were shaken to allow swelling and the swollen gel was recovered by decanting or centrifugation. Raffinate and gel volumes were calculated from weight measurements. The concentration of chemicals in the feed solution and raffinate were measured, analytical procedures are described elsewhere(22).

RESULTS AND DISCUSSION

Three kinds of experiments have been carried out to show that gels can function as size-selective extraction solvents. Batch tests were made to show that gel absorption is selective for water while rejecting high molecular weight solutes. Batch test acidification tests were designed to show how the gels can be regenerated and reused. The third kind of testing was aimed at demonstrating that the gels are sufficiently strong to be used repeatedly.

Gel Selectivity

That the gel can function as a size-selective extraction solvent is shown by the experiments reported in Table I. Gel was contacted with a series of water solutions containing different size solutes described in columns 1-3. Columns 4-5 give the feed and final (raffinate) concentrations, the increase in concentration reflects removal of water with the small amount of gel used.

The last column in Table 1 is an overall measure of extraction efficiency (E). As shown in equation 2 it is defined as the concentration difference ΔC between the initial solution and the raffinate divided by the maximum concentration difference $\Delta C_{\max}$ which would be attained if all the solute in the initial solution were recovered in the raffinate. From this definition it follows that:

$$(2) \quad E = \frac{\Delta C}{\Delta C_{\max}} = \frac{C_r/C_i - 1}{M_i/M_r - 1}$$

where

C_r = raffinate solute concentration

C_i = initial solute concentration

M_r = mass of raffinate

M_i = mass of initial solution

The quantity E has been termed the efficiency, it is really a measure of the degree to which a solute is excluded from the gel as water is absorbed. For practical applications, the degree of swelling is also important. However, the degree of swelling of polyacrylamide gels is so large that applications are likely to be limited by exclusion, not by insuf-

ficient swelling. Therefore, E is a useful parameter for characterizing performance.

The results in Table I show that solutes which are greater than 3 nm in diameter can be concentrated with an efficiency of at least 80%. These efficiencies are compromised by weak solute adsorption on the surface of the gel spheres. For example, for the 34.6 nm latex, some latex adhered weakly to the gel. When this latex was removed by washing, the extraction efficiency increased to 97%. In this sense, the gel extractions are similar to freeze-concentration techniques used in the food industry, where solutes can adhere to ice crystals.

The molecular size cut-off for rejection is dependent on the degree of cross-linking of the gel. Increased cross-linking reduces average pore size openings and hence particle rejection size range. Studies using different degrees of crosslinking will be presented at the conference.

One limitation on gel exclusion that is not shown in Table 1, involves the behavior of positively charged species. Cationic proteins like lysozyme and cytochrome C, precipitate with the gel. Thus cationic interaction may compromise separations. Interestingly, the gel's swelling seems to be largely unaffected by these reactions.

Gel Regeneration

Regeneration depends on collapsing the gel, thereby releasing the bulk of the absorbed water. The water retention properties of hydrolyzed polyacrylamide gel were tested at a series of pH levels in order to es-

establish its volume vs. pH relationship. As shown in Fig. 2, the gel volume increases sharply at pH 5-6 and goes through a soft maximum at higher pH. These pH values represent the bulk water phase and pH inside the gel may be somewhat different (27).

For a separation to be effective, the sudden increase in gel volume should occur at a lower pH than that of the solution being separated. However, the separations need not involve changing the pH of the solution. As shown in Fig. 1, the gel can be added to the solution and removed from it at the solution's pH. It is only the gel regeneration which involves adding acid or base, and not the separation itself.

The changes of gel volume shown in Fig. 2 result from a variety of thermodynamic non-idealities (21). We believe that gel ionization is the most important factor involved, equation (1), which predicts that the $(-2/3)$ power of the gel volume should vary linearly with the reciprocal of the total amount of sodium hydroxide added to the gel, should apply. This prediction is verified by the results shown in Fig. 3. At the same time, we expect that experimental results studying a broader range of variables will uncover cases where other factors are significant.

Gel Reuse

Data on repeated use of polyacrylamide gel are not currently available. However, the results obtained in earlier work using a dextran gel indicate that repeated usage is possible. Dextran gel (CM - Sephadex C-50, Pharmacia Fine Chemicals, Piscataway, NJ, which is used

as a packing for gel chromatography) was used. This material has a dry particle size of 60-120 μm , it is weakly ionic and was used as received. A dilute suspension of the 34.6 nm polystyrene latex solution (Table 1) was contacted with the dextran gel. After the gel had expanded it was removed and raffinate concentration was measured. Acid was added to shrink the dextran gel and filtered to remove released water. A drop of base was added to the gel filter cake, and again contacted with the raffinate. From a mass balance, the final raffinate concentration c after n treatment cycles, assuming perfect exclusion of the latex particles is given by equation 3.

$$(3) \quad C = \frac{m}{V_0 - nV}$$

where m is the initial mass of latex, V_0 is the initial volume of solution, and v is the volume removed by one treatment cycle of gel absorption. Thus the reciprocal of concentration c should vary linearly with the number of cycles n . The results for 12 cycles given in Fig. 4 show that this is the case for latex solutes. These results have two important corollaries. First, there is little cumulative loss due to latex adsorption on this gel. This suggests that adsorption, which is responsible for the lower separation efficiencies reported in Table I, is apparently most significant for the first cycle, and is less important as the gel is reused.

The second corollary of the results in Fig. 4 is that the gel is removing the same amount of water on the tenth cycle as on the first cycle. This implies that the gel's

swelling capacity remains essentially constant over all cycles, and hence can be reused in cyclic operation. To be sure, reuse in practice will involve hundreds of cycles and such extensive long term tests have not been made.

ACKNOWLEDGEMENTS

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

Table I. Concentration of Dilute Aqueous Solutions Using Hydrolyzed Polyacrylamide Gels.

Solute	Mol.Wgt., Daltons	Solute Size,nm	Feed Concentration(a)	Raffinate Concentration(a)	Efficiency(b)
Polystyrene Latex	—	990.0(c)	0.21	0.35	85
Polystyrene Latex	—	34.6(c)	0.91	1.40	82
Silica	—	5.0(c)	1.82	3.03	80
Bovine Serum Albumin	66,000	7.2(d)	.08	.18	93
Hemoglobin	64,500	6.2(d)	.73	1.26	91
Poly- ethylene Glycol	3000- 3700	3.8(e)	.56	1.09	91
Sucrose	342	.84(d)	1.00	1.09	6
Urea	60	.53(d)	3.00	3.00	0

(a) As weight percent.

(b) Defined by equation 2.

(c) Measured by electron microscopy.

(d) Estimated from the diffusion coefficient in water using the Stokes-Einstein equation (2).

(e) Reported by the manufacturer from light scattering.

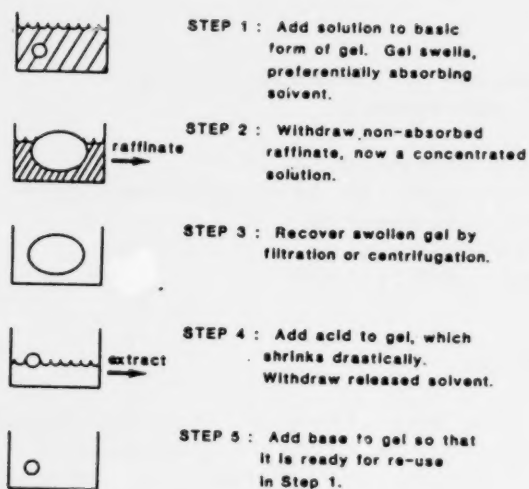


FIGURE 1

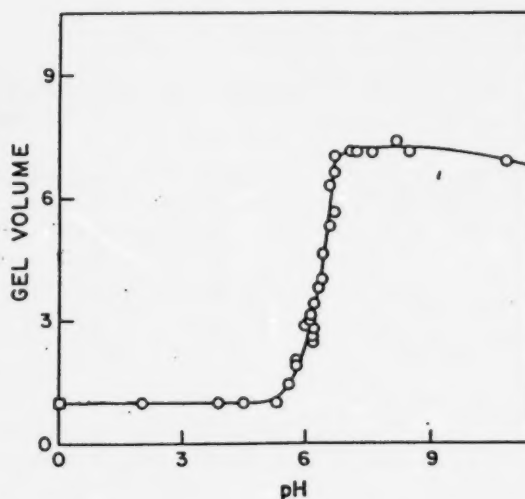


FIGURE 2

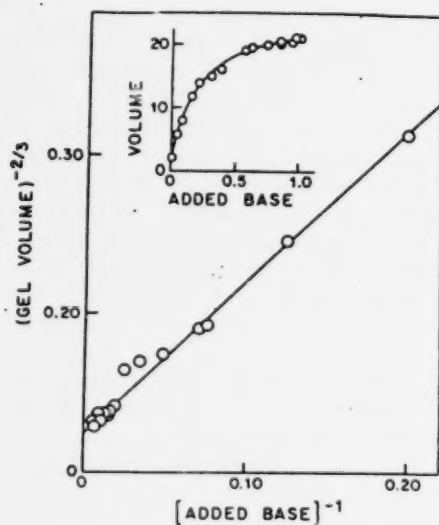


FIGURE 3

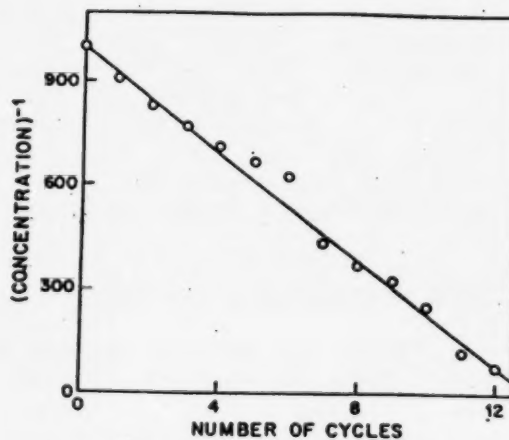


FIGURE 4

STUDIES ON THE BIODEGRADATION OF ORGANOPOLLUTANTS
BY A WHITE ROT FUNGUS

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ABSTRACT

The lignin degrading white rot fungus, Phanerochaete chrysosporium degrades a broad spectrum of organopollutants to CO₂. We have studied the ability of this fungus to degrade organopollutants using 1,1'-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) as a model compound. Like lignin degradation, the degradation of DDT requires the presence of another carbon source. In general, the total amount of ¹⁴C-DDT degraded to ¹⁴CO₂ during the 30 day incubation period increased when the glucose concentration was increased from 23 mM to 112 mM. A further increase to 224 mM did not result in a further increase in ¹⁴CO₂ production. Studies on the effect of organopollutant concentration showed that ¹⁴C-DDT degradation to ¹⁴CO₂ exhibited first order kinetics with respect to ¹⁴C-DDT concentration. Metabolism studies demonstrate that, under nutrient nitrogen limiting (2.4 mM) conditions DDT is converted to CO₂ via a pathway in which 1,1'-bis(4-chlorophenyl)-2,2,2-trichloroethanol (Dicofol) is a major intermediate. Under nutrient nitrogen sufficient conditions (24 mM), CO₂ production is suppressed and DDT is degraded via a pathway in which 2,2'-bis(4-chlorophenyl)-1,1-dichloroethane (DDD) is a major intermediate.

INTRODUCTION AND PURPOSE

Studies in our laboratory have demonstrated that the white rot fungus, Phanerochaete chrysosporium has the ability to degrade a number of recalcitrant organopollutants to CO₂ (1). Included among the compounds

degraded by this microorganism are: DDT, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), 3,4,3',4' - tetrachlorobiphenyl (3,4,3',4'-TCB), 2,4,5,2',4',5' - hexachlorobiphenyl (2,4,5,2',4',5'-HCB), 1,2,3,4,5,6-hexachlorocyclohexane (Lindane) and benzo[a]pyrene (Fig. 1). Evidence suggests that the

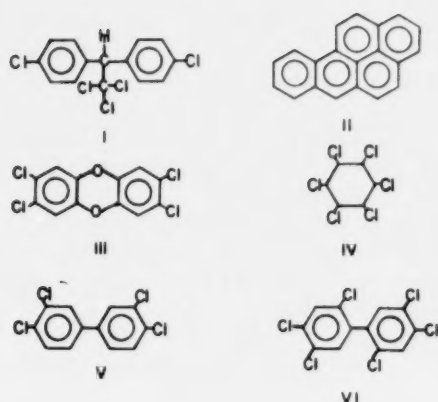


Figure 1. Structures of recalcitrant organopollutants which are degraded to CO_2 by *P. chrysosporium*. I. DDT, II. Benzo[a]pyrene, III. 2,3,7,8-TCDD, IV. Lindane, V. 3,4,3',4'-TCB, VI. 2,4,5,2',4',5'-HCB.

highly non-specific and non-stereoselective lignin degrading system of this fungus may also be active in the degradation of these organopollutants (1).

In order to be useful in systems used in the biotreatment of hazardous organic chemical wastes, a micro-organism must possess the demonstrated ability to degrade, or aid in the degradation of, recalcitrant organopollutants. It is desirable that degradation be complete and independent of the concentration of substrate. In this study we present our initial findings which focus on the optimization and control of the

degradation of recalcitrant organopollutants by *P. chrysosporium*. Because much is known concerning its biodegradation, we have elected to use DDT as a model compound in these studies.

APPROACH

P. chrysosporium (ME-446) was obtained from the USDA Forest Products Laboratory, Madison, WIS. Cultures were incubated at 39°C under 100% oxygen. The culture medium, consisting of glucose (56 mM), ammonium tartrate (12 mM) and 2,2-dimethylsuccinate buffer, pH 4.2 (100 mM) and supplemented with thiamine and trace metals has been previously described (2).

Evolution of $^{14}\text{CO}_2$ from radiolabeled organopollutants was assayed by flushing the culture with oxygen at 3 day intervals, and forcing the culture atmosphere through a scintillation cocktail which contained ethanolamine as a CO_2 trap (1,2). Typically, 50 nCi (110,000 dpm) of the radiolabeled compound was included in each culture. Time points in $^{14}\text{CO}_2$ evolution studies represent the average of four replicate cultures.

DDT disappearance and metabolite formation was assayed by GLC (1). The identity of metabolites was determined by comigration of metabolites with authentic standards and by GC-MS. Mycelium dry weights were determined after collection and drying on tared millipore filters. The data was expressed as the average $\pm$ S.D.

of three replicate cultures.

PROBLEMS ENCOUNTERED

Because the organopollutants examined in this study may not be uniformly distributed in aqueous media, sampling errors may occur when aliquots are taken when monitoring degradation or metabolite synthesis via GLC. To prevent such sampling errors entire cultures rather than aliquots of cultures are extracted and quantitated in such studies.

RESULTS

Under conditions known to promote lignin degradation by *P. chrysosporium*, we have shown that a number of recalcitrant organopollutants are also degraded to CO_2 (1). Initial $^{14}\text{CO}_2$ evolution rates varied from 0.8 pmoles of substrate converted to $^{14}\text{CO}_2/\text{day}$ for 3,4,3',4'-TCB, a PCB congener, to 13.9 pmoles of substrate converted to $^{14}\text{CO}_2/\text{day}$ for Lindane, a moderately recalcitrant alkyl halide (1). Over a 30 day period 13.3 pmoles of 3,4,3',4'-TCB and 190.8 pmoles of Lindane were degraded to $^{14}\text{CO}_2$ (1). Although these rates may appear low, two facts should be considered; 1) the conditions used were not necessarily optimal and 2) if even these rates can be maintained in a biotreatment system, aerobic composting or land farming, for example, they would be sufficient to

ensure the timely destruction of the compound undergoing degradation.

Because lignin degradation and the degradation of organopollutants by *P. chrysosporium* both appear to occur via cometabolism, we examined the effect of glucose concentration on $^{14}\text{CO}_2$ evolution from ^{14}C -DDT (Fig. 2). Standard glucose concen-

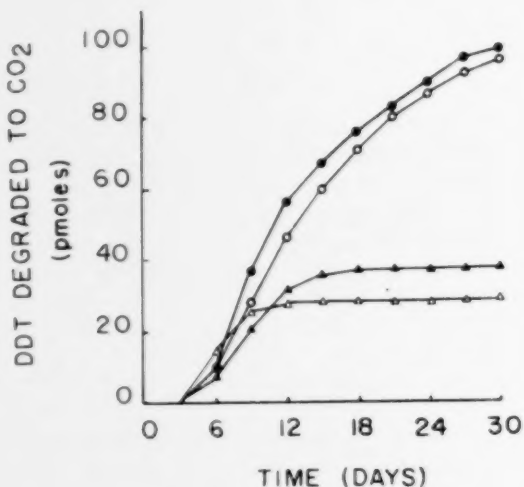


Figure 2. Effect of glucose concentration on the degradation of ^{14}C -DDT to $^{14}\text{CO}_2$ by *P. chrysosporium*. Open circle - 224 mM glucose, closed circle - 112 mM glucose, open triangle - 28 mM glucose, and closed triangle - 56 mM glucose. The concentration of ^{14}C -DDT was 0.125 μM (44 ppb).

tration in our studies was 56 mM. By increasing the concentration from 56 mM to 112 mM, a 270% increase in the total amount of $^{14}\text{CO}_2$ evolved from

^{14}C -DDT was observed (Fig. 2). However, when the glucose concentration was increased to 224 mM, no further increase was noted. In fact, a small, but statistically insignificant decrease was observed. Similarly, when the glucose concentration was reduced from 56 mM to 23 mM, a 23% decrease occurred. When the rates of $^{14}\text{CO}_2$ evolution are compared it is noted that cultures containing the higher concentrations of glucose continue $^{14}\text{CO}_2$ evolution longer than those with lower concentrations and, generally, at greater rates.

An exception to this was observed in cultures incubated with 23 mM glucose which has the highest initial rate of $^{14}\text{CO}_2$ evolution. This apparent inconsistency is in agreement with Jeffries *et al.* (3), who demonstrated that, in addition to nitrogen starvation, low levels of glucose are also effective in initiating lignin degradation. These results would suggest that lignin and DDT degradation are catalyzed by the same enzyme system or are at least under the same type of metabolic control.

In a typical $^{14}\text{CO}_2$ evolution study, the ^{14}C -radio-labeled organopollutant under study is added to the incubation mixture when the culture is inoculated with fungus at day 0. During the first 3 days of incubation a mycelial mat is quickly formed, however $^{14}\text{CO}_2$ evolution does not occur at this time (Fig. 3).

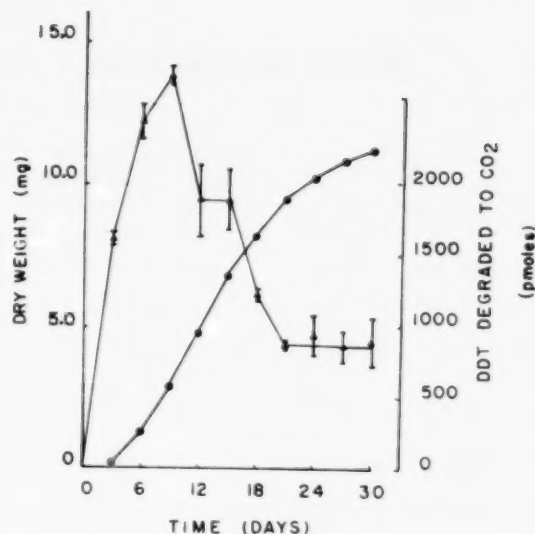


Figure 3. Time course for the growth (mycelium dry weight) of *P. chrysosporium* and its degradation of ^{14}C -DDT to $^{14}\text{CO}_2$. The concentration of ^{14}C -DDT was 4.92 μM (1.7 ppm). Triangles = mycelium dry weight, circles = CO_2 evolution.

Between day 3 and day 6, $^{14}\text{CO}_2$ evolution begins and is maximal between day 3 and day 18 after which it continues at a decreasing rate until the end of the 30 day incubation period. In studies in which the cultures were not terminated at 30 days, but were instead fortified with supplemental glucose (56 mM), the rate of $^{14}\text{CO}_2$ evolution increased and continued at a rate of no less than 4.5 pmoles ^{14}C -DDT converted to $^{14}\text{CO}_2$ per day for the duration of another

TABLE 1
EFFECT OF SUBSTRATE CONCENTRATION ON DDT DEGRADATION

Initial Concentration of DDT (ppb) (uM)	Initial Rate of Degradation of ^{14}C -DDT to $^{14}\text{CO}_2$ (pmoles/day)	^{14}C -DDT degraded to $^{14}\text{CO}_2$ during the 30 day incubation period (pmoles)	% ^{14}C -DDT converted to $^{14}\text{CO}_2$
44 (0.125)	2.8	48.0	3.8
177 (0.5)	10.5	207.1	4.1
1742 (4.92)	108.5	2047.0	4.2

30 days of incubation. Similar results have been observed with the other organopollutants we have studied.

One obvious method which might be used to increase biodegradation entails merely increasing the amount of organopollutant presented to the microorganism. Studies in which *P. chrysosporium* was incubated in the presence of increasing amounts of ^{14}C -DDT are presented in Table 1. These results indicate that increasing the concentration of ^{14}C -DDT increased the amount of ^{14}C -DDT which was degraded. When the initial rate of $^{14}\text{CO}_2$ evolution (i.e. the nearly linear rate which usually occurs between day 3 and day 18) was plotted versus ^{14}C -DDT concentration, it was demonstrated that the increase in degradation exhibited first order kinetics with respect to

^{14}C -DDT concentration over the concentration range assayed. DDT concentrations as high as 1.7 ppm (4.9 uM) did not inhibit ^{14}C -DDT degradation to $^{14}\text{CO}_2$. When the data were expressed as per cent ^{14}C -DDT degraded to $^{14}\text{CO}_2$ per 30 days (Table 1), it was found that the efficiency of degradation was approximately 4%, regardless of the initial concentration. Organopollutants are often present in contaminated soils and sediments in the parts per billion range or less. Thus it is significant that the efficiency of degradation does not appear to be concentration dependent. It should also be noted that the chemical is not required to induce the synthesis of the degrading enzymes. In fact their presence is not required at all because this enzyme system is produced in response to nitrogen starvation.

Whereas nitrogen starvation promotes both lignin and DDT degradation, excess nitrogen suppresses degradation of both chemicals as assayed by CO_2 evolution (1,2). Dicofol was found as a major intermediate of DDT metabolism during nitrogen starvation and DDD appears to be the major intermediate when nutrient nitrogen was not limiting (Fig. 4). The

Dicofol pathway predominates when degradation to CO_2 is favored while the DDD pathway predominates when degradation to CO_2 is suppressed. These results seem to have environmental relevance for DDD is a very recalcitrant environmental pollutant (4). In contrast, Dicofol does not appear to be persistent in the environment (5).

SUMMARY

These studies demonstrate that the ability of P. chrysosporium to degrade recalcitrant organopollutants may be enhanced by increasing the carbohydrate concentration of the culture, is independent of substrate concentration and is stimulated by nitrogen starvation. It also appears that there may be two pathways for the metabolism of DDT. Under low nutrient nitrogen conditions DDT is converted to Dicofol which is further degraded to CO_2 . In contrast high nutrient nitrogen conditions promote formation of DDD and further degradation to CO_2 is suppressed.

ACKNOWLEDGEMENTS

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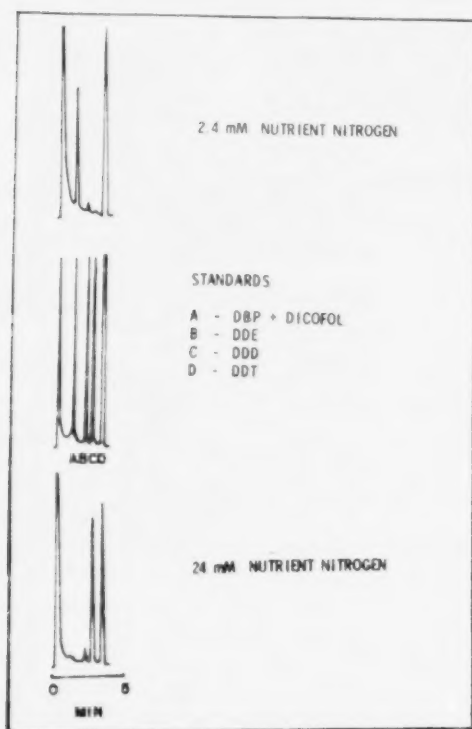


Figure 4. Gas chromatograms of hexane extracts obtained from cultures of P. chrysosporium grown in the presence of DDT (4.92 μM) under high (24 mM) and low (2.4 mM) nutrient nitrogen conditions. (DBP = 4,4'-dichlorobenzophenone).

assistance in the preparation of this manuscript.

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

ENVIRONMENTAL VAULT - A NEW CONCEPT IN LAND STORAGE

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ABSTRACT

A large volume of hazardous residues can only be treated and/or reduced in volume to a certain degree and then must be stored or disposed of in a manner that will isolate the residues from the environment for a period of time. Presently, these materials are, for the most part, being deposited in conventional below ground landfills which can create potential problems that are associated with this type of disposal.

The Environmental Vault has recently been developed as a long term storage replacement for the below ground landfill (U.S. Patent 4,464,081, August 7, 1984). The Vault is an above ground structure designed to isolate wastes from the surrounding environment and the environment from the wastes.

The major advantages of the Vault are: 1. Location is not dependent on the geology and hydrology of the site; 2. Triple liners provide failsafe groundwater and surface water protection; 3. All leachate and monitoring controls are dependent on gravity flow rather than mechanical pumping; 4. The above ground construction allows: visual observation of sides and top to check for possible malfunction of the system, easy remedial response to correct Vault problems, retrieval of the stored wastes if at some future date new technology or changing economies make recovery or future treatment possible; 5. Exemption under the Federal Act, "The Hazardous and Solid Waste Amendments of 1984" from groundwater monitoring requirements under certain circumstances.

INTRODUCTION

The need for long term storage of hazardous waste residuals is going to be with us for a long time to come. Today these residuals are being stored in and on the ground utilizing below ground landfills, pits, ponds and lagoons, as well as waste piles. The "Hazardous and Solid Waste Amendments of 1984" - RCRA Reauthorization, is going to greatly restrict what hazardous waste can be land disposed and it will also set rigid standards on the

construction and operation of disposal facilities. Because of these regulations and because of the past problems with below ground landfills and the possible liabilities that these fills may present, it is doubtful whether any new below ground landfills will be permitted in the United States. This, along with the fact that many presently permitted landfills are either nearing capacity or are being phased out because of the new forthcoming RCRA regulations, presents a major problem in hazardous waste management.

Inorganic residuals, some organic residuals, contaminated soils and incinerator ash and sludges require long term storage, and if the present storage options are restricted and/or eliminated, new techniques are going to be required to manage these types of waste. The need for secure long term storage, in fact, is going to increase over the next decade as we remediate our problems of the past through Superfund and the private sector. A large percentage of the contaminated material at these sites is soil, with relatively small concentrations of toxic pollutants. These soils, and the possible leachate from these soils, must be isolated from the groundwater. However, it makes no sense to transport this contaminated soil, possibly hundreds of miles, and deposit it in an existing below ground landfill that could be the next generation of Superfund activity. What is needed is a secure storage design that can be easily constructed at the site that is to be remediated, that is tolerant of a variety of hydrogeological conditions, is cost effective, and will protect the environment from the waste and the waste from the environment.

PURPOSE

The Environmental Vault is a new development that satisfies these needs. It is an above ground structure that is designed for long term storage of hazardous wastes. It protects the wastes from precipitation, ground and surface waters, and it protects the ground and surface waters from the wastes and any leachate that is produced. Because the Vault is above ground, it can be constructed at sites with a variety of hydrogeological conditions.

Other advantages of the Vault are:

- A triple liner system for maximum protection.

- All monitoring and leachate systems are gravity fed and not dependent on mechanical devices.

- Visually inspected for possible problems.

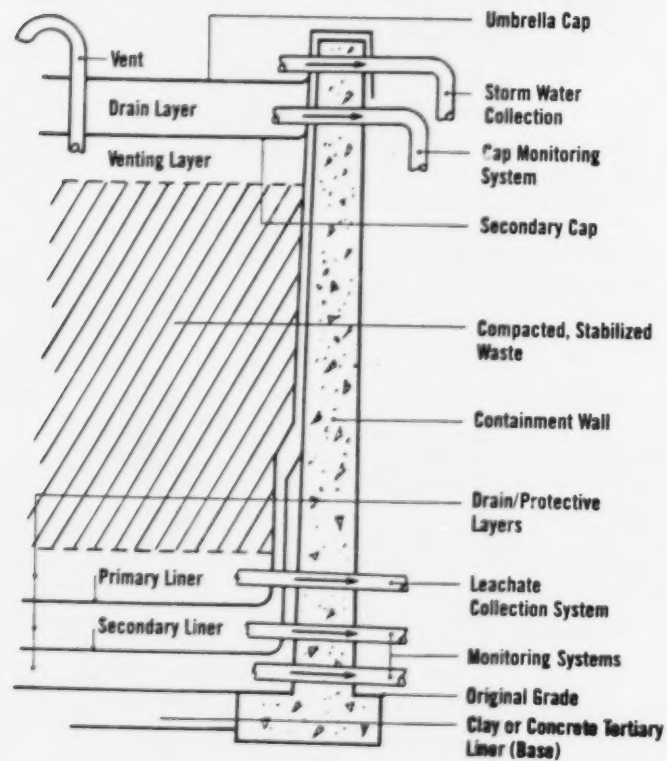
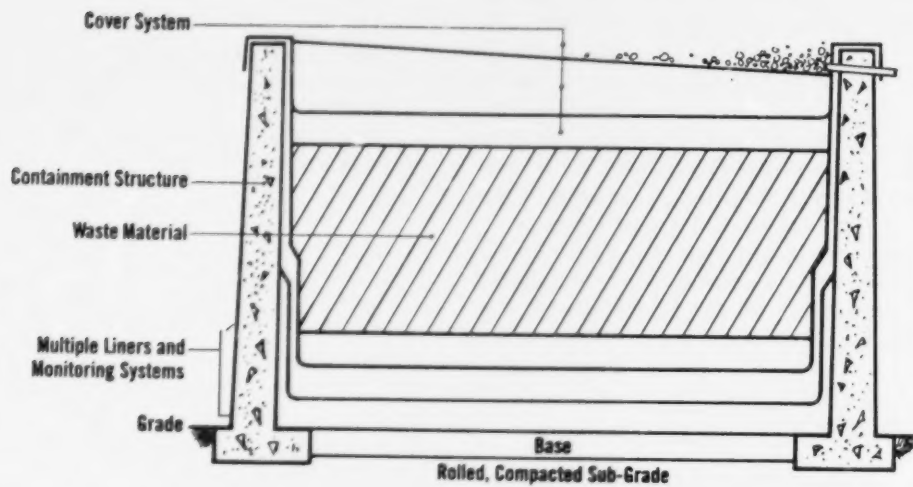
- Stored wastes can be retrieved in the future if new technology or economic considerations make further treatment or recovery practical.

In constructing the Vault, the site is first prepared as you would in building a house on a concrete slab foundation. Next a concrete base is constructed with concrete walls using state-of-the-art civil engineering construction techniques to insure a secure structure. This outer concrete construction forms the containment structure and, after it has been properly sealed, also becomes the tertiary liner. Secondary and primary liner systems are placed over the base, with interspaced drain zones between the liners to catch and drain any leachate formation. The materials of construction of the primary and secondary liners will be determined by the nature of the wastes being stored, however, as a general rule a 100 mil high density polyethylene liner will be used.

The drain zones between the waste and the primary liner, and between the primary, secondary, and tertiary liners incorporate a monitoring pipe network that through gravity flow collects and delivers any leach to leachate collection tanks that can be instrumented to measure the volumes of any liquids that are collected. This system will not only collect and store leach contained by the primary liner, but monitor the integrity of the liners by detecting any liquid flow between the liners.

Environmental

Vault



The Vault cap includes two polymer liners, namely an umbrella cap and a secondary liner. A collection system is installed above the umbrella cap for stormwater collection and a second collection system is installed between the umbrella cap and the secondary liner so as to monitor the integrity of the umbrella cap. A ballast material or topsoil and cover combine to serve as an excellent water runoff system and also provide an aesthetically pleasing appearance. The surface of the cap could, however, be paved if this would serve a purpose. A vent system is designed to collect any gases produced by the wastes and vents them through absorption mediums such as carbon and then to the atmosphere.

The wastes that are deposited in the Vault are first treated to stabilize and reduce their leachability. They are further compacted when they are placed into the Vault.

The Vault can be constructed in a variety of sizes. An optimum size is an acre to one and a half acres in area and 20 to 25 feet in height, which provides a volume of 30,000 to 45,000 cubic yards. If the demand warrants it, several of these Vaults can be constructed at a given site.

CONCLUSION

In review, long term storage of hazardous wastes will be needed in this country for many years to come. In fact, with the remediation of sites that have been polluted in the past, needs for this type of storage will increase over the next decade. New RCRA regulations are going to restrict the construction and operations of land disposal/storage facilities. The Environmental Vault is a new technique for environmentally secure

storage. With the use of the Rollins Environmental Vault the problem hazardous waste site can be cleaned up and made available for other uses. In contrast, when groundwater containment barriers or similar remedial actions are used, the site remains unusable for other purposes. Using vegetation and landscaping techniques, the land is freed for alternative uses.

Disclaimer

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IN SITU TREATMENT TECHNOLOGIES AND SUPERFUND

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ABSTRACT

In situ systems for treating waste deposits involve three essential elements: selection of a chemical or biological agent which treats the waste, a method for delivery of the reactant to the deposit and a method for recovery of the reaction products or mobilized waste.

Four methods for in situ treatment (or extraction) of subsurface organic wastes are reviewed: biodegradation, surfactant-assisted flushing, hydrolysis and oxidation. These methods have potential application to certain organic wastes, and each has potential drawbacks. Biodegradation and surfactant-assisted flushing are among most promising insitu treatment methods. An example of the use of in situ biodegradation is provided.

The underlying limitation to use of the technologies associated with in situ treatment of or deposits is that these methods are often in an experimental stage of development. This finding frustrates efforts to systematize selection of reagent and delivery and recovery systems and emphasizes the need for laboratory simulation and testing prior to implementation. Each site at which in situ treatment is considered becomes, in essence, a research project. Although the need for in situ treatment methods is underscored by the expense and impacts associated with such practices as excavating, transporting and landfilling waste deposits, the use of in situ methods on a large scale is hampered by the lack of field experience. There is little incentive for site managers to consider their use. The tasks which could be undertaken at the programmatic level to enhance the development and implementation of in situ treatment methods for the remediation of hazardous waste sites are discussed.

INTRODUCTION

In December 1982, Envirosphere Co. a division of Ebasco Services Inc. was selected by JRB Associates to undertake a project entitled "Evaluation of Systems to Accelerate Stabilization of Waste Piles or Deposits". The EPA project officer is Dr Walter Grube of HWERL. The EPA project number is 68-03-3113, Task 37-2.

This project represents Phase I of a two phase scope of work whose purpose was to document the feasibility of engineered approaches to treating subsurface waste deposits via the application of in situ methods. Phase I concentrated on applications of available technology and examined the limitations imposed on their use by site and waste specific characteristics. A future phase of the project, Phase II, is expected to under-

take bench scale or pilot studies to expand the data base available to potential users of in situ methods.

APPROACH

Envirosphere pursued a six part program of investigation which consisted of a literature review, a definition of the capabilities and limitations of delivery, recovery and treatment technologies, visits to sites where remedial activities were underway, a definition of important site and waste characteristics, and an evaluation of remedial technologies. The available data were evaluated to determine classes of organic chemicals amenable to treatment by various potential in situ treatment methods. Potential delivery and recovery systems for these treatment agents were then evaluated with respect to site hydrogeologic characteristics.

Envirosphere then developed a guidance manual which identified combinations of delivery/recovery technologies and reagents which have a reasonably high or clearly low probability of success.

PURPOSE

- 1) To present a concise summary of EnviroSphere's findings relative to selection of an in situ treatment option,
- 2) To illustrate an example of a successful application of in situ techniques,
- 3) To analyze the programmatic barriers to implementing in situ treatment technologies within the Superfund program.

With respect to the Phase I effort, EnviroSphere has submitted its draft final report covering the evaluation of in situ treatment systems to EPA for final approval. This document is expected to be published late in 1985. The report is a guidance document which will assist to site managers in choosing remedial action, involving in situ treatment especially in the early phases of technology selection within the FS process.

PROBLEMS ENCOUNTERED

In the study of in situ treatment of hazardous waste piles or deposits one encounters a significant difficulty which prevents the drawing of many generalizations from the extant literature. Each in situ application resembles a research effort which must be customized to the site and waste characteristics. The essence of a successful application of an in situ method is the performance of a treatability study designed to account for the peculiarities of the waste and treatment reagent combination as well as the unique geohydrological characteristics of the site. Since treatability studies cannot exist for the generalized case, almost all conclusions to be drawn from the literature survey were necessarily based upon engineering judgement. Verification of hypotheses by reference to documented field experience was not feasible in most situations.

Another problem encountered was the degree of homogeneity of the waste deposit. Subsurface deposits contained in drums or within non-uniform formations which impede the flow of water-borne reagents cannot be considered as realistic candidates for in situ treatment. The experience that exists strongly suggests that the greatest in situ success will be with a plume or a spill situation rather than with a source deposit itself.

RESULTS

There are many different viewpoints as to what constitutes application of in situ methods. A workable definition is that insitu treatment means treatment of contaminated soil without excavation. This definition encompasses four different possibilities for in situ methods: Treatment involving the inground transformation of contaminants to harmless products; Stabilization involving the inground chemical immobilization of contaminants; Solidification involving the in-ground physical immobilization of contaminants and Extraction involving a subsurface displacement followed (usually) by chemical treatment on the surface.

This paper reports on in situ treatment methods and certain extractive methods applicable to target organic contaminants.

Biological Renovation of Waste Deposits

Aerobic and anaerobic bacteria, fungi, actinomycetes, algae and cyanophytes (blue-green algae) have all been shown capable of degrading many classes of organic chemicals. These microbes include natural microbial populations, adapted microbial cultures and potentially bioengineered microbial strains (1,2). Once the extent of the contamination and its chemical characterization have been determined, the proper microorganisms (or groups of microbes) may be identified and developed. The identification of the proper agents for waste site renovation is based upon past experience, laboratory screening, and onsite pilot-scale tests.

To date, aerobic bacteria such as *Pseudomonas* have been most commonly used for in situ biodegradation of contaminants. These organisms can potentially completely convert the organic compounds to CO₂ and water, and do not produce H₂S or methane as reaction products. However, anaerobic bacteria are important for the biodegradation of pesticides and halogenated organics. Organic contaminants that have been successfully treated by biodegradation include phenols, gasoline and other petroleum products, methylene chloride, alcohols and acetone (3, 4).

In the process of designing the microbial waste treatment system, one must determine the oxygen, emulsifier (if the wastes are insoluble) and fertilizer requirements for optimum waste treatment rates. Microbial agents require the maintenance of sufficient concentrations of nitrogen, phosphorus and trace elements, and a pH range that will support their growth. The levels of these factors at the site should be determined during the site investigation; the need for additional fertilizers or buffers required to support microbial growth can then be identified.

Biological renovation of subsurface waste deposits poses problems relating to oxygen supply, temperature, permeability and accessibility not encountered with surface disposal sites. Injection wells may be established into and below the waste site to deliver a fertilizer and oxygen supply (5). Oxygen sources would include injectable solutions of peroxides, oxygen-charged water produced by ozonation (6), or direct sparging of air into the groundwater (3). Recovery wells or trenches should be situated at points peripheral to or downgradient of the waste deposit. Flow patterns established between injection and recovery wells should be planned to aid in confining the waste during the renovation process. In this way groundwater plumes that may be migrating from the site can be renovated as well.

Application of Hydrolysis to Waste Deposit Stabilization

Hydrolysis is a chemical reaction involving the cleavage of a molecular bond by reaction with water. The rates of hydrolysis for some compounds can be accelerated by altering the solution pH, temperature, solvent composition, or by introducing catalysts. For in situ treatment, alteration of pH, particularly raising the pH (base-catalyzed hydrolysis), is the most promising approach. The range of chemical classes potentially treated by base-catalyzed hydrolysis includes amides, esters, carbamates, organo-phosphorus compounds, pesticides and herbicides. Base catalyzed hydrolysis has been successfully used for treatment of surface spills of acrylonitrile and pesticides (7).

The primary design concern for implementation of base-catalyzed hydrolysis within a waste deposit will be the production and maintenance of high pH (9 to 11) conditions with saturation or high moisture content in the waste deposit. For shallow subsurface or surface deposits, surface application of lime, sodium carbonate or sodium hydroxide followed by surface application of water may be appropriate.

For deeper deposits, subsurface delivery or injection of alkaline solutions may be required.

Potential for In Situ Oxidation of Waste Deposits

The potential application of three oxidants (ozone, hydrogen peroxide, and hypochlorites) to waste deposits was evaluated. Although in widespread use in surface water treatment applications, significant problems may preclude their effective implementation as in situ treatment agents for waste deposits.

Hypochlorite reacts with organic compounds as both a chlorinating agent and an oxidizing agent. Documentation on the effectiveness of hypochlorite as an oxidizing agent for organic materials is extremely limited. Hypochlorite additions may lead to production of undesirable chlorinated by-products (e.g., chloroform) rather than oxidative degradation products. Therefore the use of hypochlorite for in situ treatment of organic wastes is not recommended.

While ozone is an effective oxidizing agent for many organic compounds in wastewater treatment applications, its relatively rapid decomposition rates in aqueous systems, particularly in the presence of certain chemical contaminants or other agents which catalyze its decomposition to oxygen, preclude its effective application to subsurface waste deposits. The half-life of ozone in groundwater is less than one-half hour (10). Considering that flow rates of water through waste deposits are likely to be on the order of inches/hour or less, it is unlikely that effective oxidant doses of ozone can be delivered outside of the immediate vicinity of the point of application. Successful use of ozone for in situ chemical oxidation is unlikely. However, ozonation has been used successfully to supply oxygen for microbial biodegradation, and to chemically oxidize complex organics in a surface reactor to simpler compounds that are more readily biodegradable (6). This use of ozone as a supplementary treatment for biodegradation seems promising.

Hydrogen peroxide is a weaker oxidizing agent than ozone; however, its stability in water is considerably greater. Since decomposition of hydrogen peroxide to oxygen may be catalyzed by iron or certain other metals, effective delivery of hydrogen peroxide throughout an entire waste deposit may be difficult or impossible because of the relatively low transport velocities achievable in waste deposits. Prior to consideration of hydrogen peroxide as an in situ treatment method, it will be necessary to investigate the stability (or rate of decomposition) of hydrogen peroxide in the specific waste deposit matrix. Hydrogen peroxide may also be used as an oxygen source for microbial biodegradation (9).

Surfactant-Assisted Flushing or Solubilization of Wastes

Flushing or mobilization of wastes can serve two purposes: to promote the recovery of wastes from the subsurface for treatment on the surface, or to solubilize adsorbed compounds in order to enhance the rate of other in situ treatment techniques (such as biodegradation or hydrolysis). Flushing or mobilization using water alone may be sufficient for relatively soluble compounds such as phenols; however, the use of surfactants will be required for significant solubilization of insoluble (hydrophobic) compounds.

Surfactants (surface active agents) are a class of natural and synthetic chemicals which promote the wetting, solubilization, and emulsification of various types of organic chemicals. A simple approach to evaluating the potential use of surfactants in organic waste recovery involves consideration of the aqueous solubility or octanol-water partition coefficient, K_{ow} . Surfactants would be most effective in promoting the mobilization of organic compounds of relatively low water solubility and high K_{ow} values.

Laboratory tests suggest that surfactants may enhance the recovery of subsurface gasoline leaks by groundwater pumping, and promote the mobilization of crude oil and PCBs from soils (10).

However, certain environmental factors may reduce the in situ effectiveness of surfactants. These include precipitation of the surfactant by groundwater with high TDS or alkaline earth cation concentrations (Ca, Mg); reduction of surfactant effectiveness due to non-optimal pH or temperature; or adsorption of the surfactant by soil particles, negating its solubilizing properties. Nevertheless, the use of surfactants either alone (to flush otherwise insoluble organics) or in combination with other treatments (to solubilize the waste materials and thereby promote biodegradation) is a promising avenue for further research.

The potential applicability of the four above treatment technologies versus a wide array of target organic compounds is presented in Table 1.

Case History - Biodegradation

Probably the most successful insitu method for remediation of soil contamination and groundwater restoration is biodegradation. Success has been reported (4) in treatment of spills and groundwater contaminated by methylene chloride, ethylene glycol, isopropanol, phenolic compounds, acetone and tetrahydrofuran. Other references cite successful attempts using biodegradation in treatment of methylene chloride (3), and petroleum based hydrocarbons and hexacyanoferrate ion (4).

One of the best documented case histories on biodegradation is the case at Biocraft Laboratories in Waldwick, N.J. (11). Biocraft Laboratories is a small synthetic penicillin manufacturing plant located on a 4.3 acres site in an industrial park in Waldwick, N.J. In August 1975, contamination was observed in a small creek which was traced to a storm sewer draining the site and subsequent investigations revealed a leak in underground storage process lines connecting solvent storage facilities. The inventory of contaminants estimated to have escaped into the environment is presented in Table 2.

TABLE 2. BIOCRAFT SITE ESTIMATED CONTAMINATION INVENTORY IN SOILS (3)

Methylene Chloride	CH ₂ Cl ₂	181500 lb
N-Butyl Alcohol	C ₄ H ₁₀ O	66825 lb
Dimethyl Aniline	C ₈ H ₁₁ N	26300 lb
Acetone	C ₃ H ₆ O	10890 lb

An approximately 1.75 acre area and 1200 yd³ of soil were contaminated. A municipal well located about 1000' east of the property was believed to be in jeopardy of contamination. Biocraft undertook an extensive groundwater profiling, sampling and analysis program. A total of 22 wells with continuous recorders were constructed on the site and a detailed description of the groundwater regime was generated.

A number of alternative response technologies were considered including collecting and treating all discharge from the storm sewer; isolating the storm sewer from the contaminated flow by grouting pipe joints, pipe resleeving or pipe replacement; surrounding the area with grout or a slurry cutoff wall or excavating the entire contaminated soil column under the site. Selective pumping of groundwater and offsite disposal was chosen as the remedial method. However, to undertake this remedial measure, contaminated groundwater had to be shipped off-site for disposal at an average estimated cost of \$0.35 per day (12).

Driven by the high cost and ongoing uncertainty associated with the effectiveness of the initial remedial method in treating the contaminant, Biocraft developed the selected alternative: collecting the contaminant plume down-gradient in a slotted pipe collection trench, treating the collected groundwater in a surface aerobic biological treatment system, injecting the treated "bioactive" water upgradient in two slotted pipe recharge trenches and enhancing insitu biological treatment in the subsurface through injection of air in equally spaced air injection wells.

A detailed description of the system which has been patented by Groundwater Decontamination System, a subsidiary of Biocraft Laboratories, appears in reference 11. Of considerable interest is the performance of the system reported to date. Tables 3 and 4 provide summaries.

TABLE 3. AVERAGE REMOVAL EFFICIENCY OF AEROBIC TREATMENT SYSTEM (3)

Target Contaminant	Reported Removal Efficiency
Methylene Chloride	98%
n-Butyl Alcohol	98%
Acetone	97%
Dimethyl Aniline	93%

TABLE 4. PRE-AND POST-TREATMENT RESULTS FOR METHYLENE CHLORIDE AT BIOGRAFT SITE (3)

Well	1981 (Pre)	1983 (Post)
4A	67 ppm	ND (=Not Detected)
25	260 ppm	ND
26	360 ppm	8 ppb
31	78 ppm	10 ppb
P-13	989 ppm	ND
P-30	880 ppm	23.5-64 ppm
P-32A	305 ppm	305-182 ppm

It is reported that the overall remediation at the site is proceeding successfully (13) and that 60% of the treatment occurs above ground (in the reactor) and that 40% occurs below the surface. It is estimated that the system will require 5 years to complete the cleanup at the Biocraft Site compared with 15-20 years using the initial groundwater withdrawal and off-site treatment alternative.

Capital and Operating and Maintenance costs are documented at \$926K and \$226/day respectively (11). The total cost at the Biocraft Site using the system now in operation is estimated to be 1/4 of the total cost which would be incurred via the initial remedial measure (pumping and offsite disposal) (13).

This one example points up the potentially significant advantages of in situ treatment. However, an important point to consider is that the preliminary research and pilot studies aspect of the overall capital cost was about \$450,000 or 1/2 of the total capital cost. Thus, in order to realize the ultimate savings, a significant investment was required in site specific research. The necessity for significant treatability studies and research is a fundamental element in virtually all in situ remediations and represents a significant risk in potential time and money to the prospective user of in situ methods. Some of the barriers to employing in situ technologies for remediation at hazardous waste sites are now discussed along with suggested solutions to these implementation problems.

NON-TECHNICAL CONSIDERATIONS

The preceding sections presented several ambitious in situ treatment systems for application at hazardous waste sites. The primary objectives behind EPA's funding of this type of research and development program is to accelerate the rate of technology development and transfer in this area and also to promote its adoption at actual sites. However, in addition to the numerous technical challenges to be met in developing any of the technologies discussed in this article, there are others which are non-technical in nature that must be met to enhance the chances of developing and applying these emerging technologies to hazardous sites. The following paragraphs briefly outline these major challenge areas and suggest general approaches to dealing with them.

Funding

Few technologies have been evaluated in the context of a site-specific application. Because of the uncertainty involved in applying an innovative remedial approach, there will always be reluctance to test their feasibility. In the case of Superfund sites, the skepticism is enhanced by the political and economical restraints which would make it impossible for a regulatory

agency, the public, and engineers to risk pursuing what is perceived as an "R&D study of an unproven technology".

One major area of improvement is funding. Funding by EPA and other government agencies (e.g., NSF), as well as industrial trade organizations (e.g., CMA) is recommended to accelerate the development and application of the subject technologies. Specifically, the following are suggested:

Funding of Superfund site-specific R&D projects should be initiated and expanded. It is recommended that considerations be given to hazardous waste sites that are not on the NPL. This would enhance the chances of a feasibility study being conducted on sound technical bases that are not complicated by the typical financial, political and institutional considerations that are characteristic of NPL site work.

Congress and EPA should work out a formula to ensure that an R&D budget for in-situ treatment technologies is established in linkage with the budget for the REM programs which have the overall responsibility for ascertaining the need for, and utility of, these innovative remedial technologies.

Institutional Framework

The objectives and approaches to site remediation within the context of Superfund, is defined by EPA in the National Contingency Plan (NCP), and substantially shaped by various articles in the NEPA, CWA, RCRA and TSCA regulations. These environmental regulations and guidelines form the basis for assessing environmental and health risks, development and evaluating remedial measures, but most importantly ranking and selecting the remedial alternatives. The general scope, specific contents, and enforcement status of these regulations affect in many ways the perceived urgency of applying in situ treatment methods at hazardous sites and, in most cases, the feasibility of their design, permitting, implementation and operations. Cases in point: In the early years of Superfund, little emphasis was placed on considering

in situ treatment techniques at NPL sites. This is attributed primarily to the perception that the RCRA regulations regarding secured landfilling of hazardous waste were reasonably achievable. As additional experience with such landfills was gained, technical guidance, permitting, and later on RCRA amendments, tended to impose substantial constraints on land disposal of hazardous wastes. As a result, a great deal of research, development and implementation is needed regarding in situ treatment methods. It is believed that EPA and state agencies will, and should, continue to limit secured landfilling. This, coupled with an intensified enforcement of the regulations, should increase the attention given to the development and application of the in situ treatment technologies.

The experience with remedial site projects indicates that permitting of an in situ treatment operation and associated field pilot studies can be critical to the successful development of a process. The uncertainty associated with subsurface geochemical and contamination conditions pose real difficulty with regard to providing specific effluent and other data typically required in a permitting process. Moreover, the complexity of these technologies and the permitting process itself, are expected to result in delays that can substantially hinder cost-effective feasibility demonstrations, particularly at NPL sites. It is therefore recommended that consideration be given to develop and implement a more flexible permitting policy with regard to field testing and operation of in situ treatment technologies.

The financial resources, or sometimes the perception thereof, required for the development, and tailoring to a site condition, of an in situ treatment process can be great. This can be a hindrance with respect to getting private responsible parties (PRPs) to "take a chance" on trying to develop and apply an in situ treatment method at a given site. It is suggested that efforts be made to creating effective incentives for PRPs to pursue innovative remedial approaches.

agency, the public, and engineers to risk pursuing what is perceived as an "R&D study of an unproven technology".

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In the early years of Superfund, little emphasis was placed on considering

in situ treatment techniques at NPL sites. This is attributed primarily to the perception that the RCRA regulations regarding secured landfilling of hazardous waste were reasonably achievable. As additional experience with such landfills was gained, technical guidance, permitting, and later on RCRA amendments, tended to impose substantial constraints on land disposal of hazardous wastes. As a result, a great deal of research, development and implementation is needed regarding in situ treatment methods. It is believed that EPA and state agencies will, and should, continue to limit secured landfilling. This, coupled with an intensified enforcement of the regulations, should increase the attention given to the development and application of the in situ treatment technologies.

The experience with remedial site projects indicates that permitting of an in situ treatment operation and associated field pilot studies can be critical to the successful development of a process. The uncertainty associated with subsurface geochemical and contamination conditions pose real difficulty with regard to providing specific effluent and other data typically required in a permitting process. Moreover, the complexity of these technologies and the permitting process itself, are expected to result in delays that can substantially hinder cost-effective feasibility demonstrations, particularly at NPL sites. It is therefore recommended that consideration be given to develop and implement a more flexible permitting policy with regard to field testing and operation of in situ treatment technologies.

The financial resources, or sometimes the perception thereof, required for the development, and tailoring to a site condition, of an in situ treatment process can be great. This can be a hindrance with respect to getting private responsible parties (PRPs) to "take a chance" on trying to develop and apply an in situ treatment method at a given site. It is suggested that efforts be made to creating effective incentives for PRPs to pursue innovative remedial approaches.

Superfund's Programmatic Considerations

Several issues related to the scope and approach of the Superfund Program are noteworthy as they relate to development and application of innovative remedial technologies. The following paragraphs focus on the remedial investigation/feasibility study (RI/FS) stage of a site's remedial response chronology.

The basic planning process of an RI/FS needs to be reconsidered to enable the early identification and detailed evaluation of innovative in situ treatment technologies. These are currently eliminated at the initial screening stage, primarily on the grounds of inadequate definition of engineering and environmental performance characteristics.

Exceptions must be taken to the established "rules of thumb" applicable to "guesstimating" preliminary budgets and schedules for RI/FS tasks when an innovative technology is considered. Depending on the site conditions and the particular technology, both budget and schedule of an RI/FS would be extended to allow for the requisite site and bench scale studies.

A practical rational approach needs to be developed to perform cost-effectiveness evaluation of competing remedial alternatives which does not penalize emerging in situ treatment technologies on the basis of cost and lack of track record.

Community Relations Program (CRP) for a RI/FS that considers an innovative in situ remedial technology will involve a higher level of sensitivity and participation from the public. This must be carefully planned for in advance since the public perception of these remedies will often be that "the waste, and associated hazards, are staying in the community." The program should also highlight the growing limitations and restrictions associated with secured landfilling and other conventional remedies.

CLOSING

The application of in situ treatment technologies to hazardous waste site represents a technical, programmatic and economic challenge in which significant research expense must be incurred at early stages in the remedial action. The existing early experience points to cost effective possibilities especially for plume and spill remediation. In situ treatment represents one of the possibilities for escaping from the secured landfill as the ultimate repository for hazardous waste. Changes as suggested above in the approach to remediation at the program and regulatory level are needed to nurture technical advances in situ technologies.

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

TABLE 1. POTENTIAL APPLICATIONS OF TREATMENT METHODS TO WASTE CONTAMINANTS

Chemical Class	Bio-degradation	Hydrolysis ⁽¹⁾	Oxidation ⁽²⁾	Water Flushing ⁽³⁾	Surfactant Flushing ⁽³⁾
Aliphatic Hydrocarbons	+	-	+	-	+
Alkyl Halides	+	+	?	-	?
Ethers	+	-	?	-	+?
Halogenated Ethers and Epoxides	+	+	?	?	?
Alcohols	+	-	+	+	-
Glycols/Epoxides	+	-/+	+	?	?
Aldehydes, Ketones	+	-	+	+?	-?
Carboxylic Acids	+	-	+	?	?
Amides	+	+	+	?	?
Esters	+	+	?	?	?
Nitriles	+	+	+	?	?
Amines	+	+	+	+?	-?
Azo Compounds, Hydrazine Derivatives	+	-	+	?	?
Nitrosamines	+	-	+	?	?
Thiols	+	-	+	?	?
Sulfides, Disulfides	+	-	+	?	?
Sulfonic Acids, Sulfoxides	+	?	?	?	?
Benzene & Substituted Benzene	+	-	+	-	+
Halogenated Aromatic Compounds	+	-	?	-	+
Aromatic Nitro Compounds	+	-	+	?	?
Phenols	+	-	+	+	-
Halogenated Phenolic Compounds	+	-	+	?	?
Nitrophenolic Compounds	+	-	+	?	?
Fused Polycyclic Hydrocarbons	+	-	+	-	+
Fused Non-Aromatic Polycyclics	+	-	+	-	+
Heterocyclic Nitrogen Compounds	+	-	+	-	+?
Heterocyclic Oxygen Compounds	+	-	+	-	+?
Heterocyclic Sulfur Compounds	+	-	?	-	+?
Organophosphorus Compounds	+	+	?	?	?
Carbamates	+	+	?	?	?
Pesticides	+	+	?	?	?

(1) Based upon calculated half-lives for base catalyzed at pH 9 to 11.

(2) Based on oxidation of chemicals in water and wastewater by H_2O_2 .

(3) Based upon aqueous solubility and octanol/water partition coefficient (K_{ow}).

+ = can be used
 - = cannot be used
 +? = probably can be used

? = further research needed
 -? = probably cannot be used

PUMPING TOXIC AND RADIOACTIVE FLUIDS WITH AIR LIFTS

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ABSTRACT

Extreme reliability is often required of pumps handling highly toxic or radioactive liquids because of the problems associated with maintaining or repairing the pumps. Moreover, many of these pumps will be in remote locations, and will be used intermittently, so that simple control and start-up is an advantage. Air lifts offer an attractive solution to such pumping problems, but few theoretically sound design techniques for air lifts have appeared in the literature. Operating curves show the delivered rate of fluid as a function of the air flowrate used; for relatively short pumps, these curves can be constructed by assuming an average air flowrate in the pump, and performing a momentum balance over the height of the pump, equating the sum of the hydrostatic head, frictional losses and acceleration terms with the pump submergence. This approach is valid for typical pumps of up to 30 meters in height, and can be used to analyze the effect of design variables on the liquid flowrate.

INTRODUCTION

Uses of air lifts

Air lifts provide a simple, reliable method of pumping radioactive or highly toxic liquids because they require remarkably little maintenance. To date these pumps have been used for mine dewatering, ocean mining, dredging, effluent aeration and for flotation of coal. Having no moving parts, an air lift is resistant to damage by solids or particles in the liquid, unlike centrifugal pumps which suffer impeller erosion, so that air lifts can be used to raise difficult slurries or to desludge effluent ponds.

Air lift description

An air lift pump is simple and inexpensive to construct, consisting of a vertical pipe partly submerged in liquid, or equivalently fed liquid at some head from a tank. In figure 1 the distance ($x_1 - x_0$) is called the submergence, and the distance ($x_2 - x_1$) is termed the lift. Usually the pressure in the tank, P_1 , and pressure in the header pot, P_2 are equal (often being atmospheric pressure). In cases where they are not equal, the effective submergence of the pump will be altered. Air is introduced near the base of the pipe, and a buoyant air-liquid mixture is carried up the pipe to a header pot, where the gas and liquid disengage. Generally the air and liquid flowrates are such that the mixture is in "slug flow"

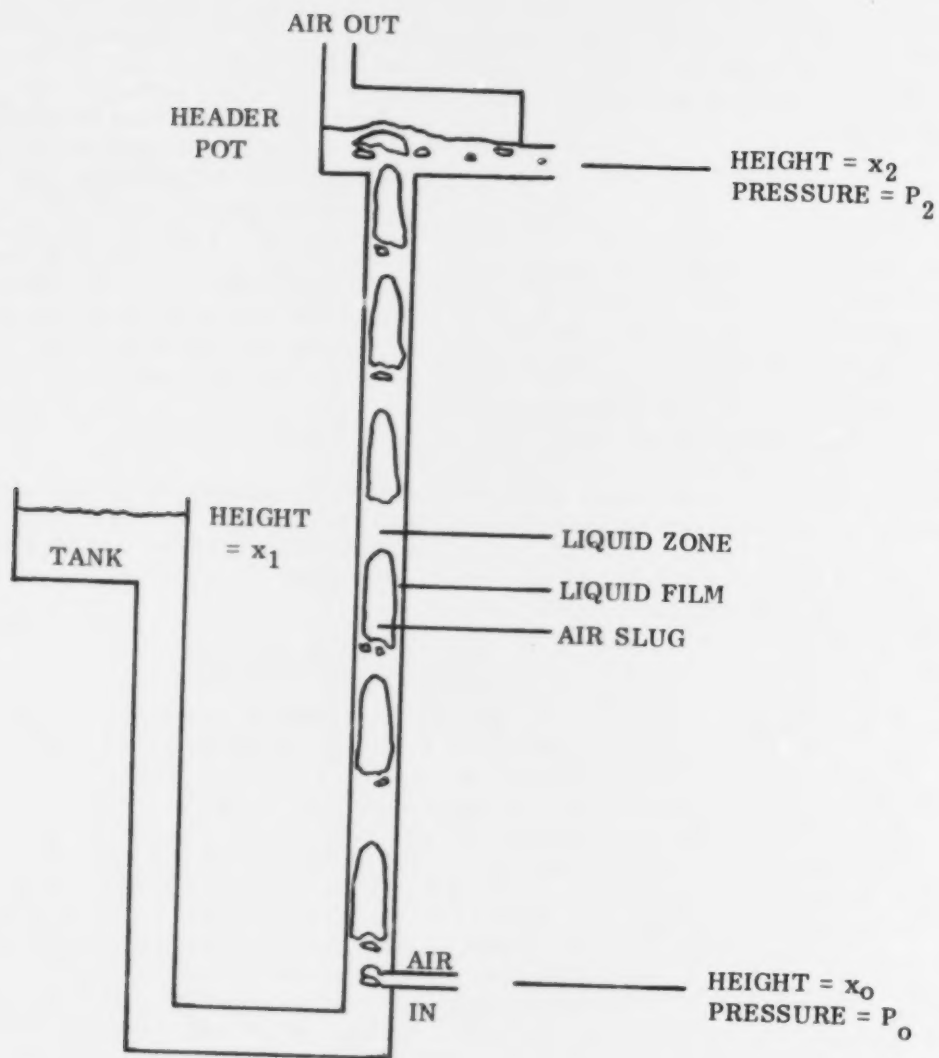


Figure 1: Air Lift Pump.

(1,2,3), which consists of alternating plugs of liquid and large air bubbles spanning almost the whole pipe diameter. The energy source for the pump is the compressed air, which expands over the pump height; liquid flowrate is controlled by varying the air rate, so that remote operation is readily implemented.

PURPOSE

This paper seeks to present a reliable design procedure to encourage the use of air lifts in handling dangerous liquids and slurries. A well designed air lift pump can offer energy efficiencies of over 50%, which many specialist pumps cannot match. Despite the fact that air lifts have already been used at nuclear reprocessing plants (4), and that air lifts with total heights from a meter to several hundred meters have been demonstrated successfully in a wide range of industries, air lifts do not currently enjoy the application that they ought. This is because reliable design techniques have received insufficient attention in the literature. Current engineering handbooks still recommend empirical or semi-empirical equations, and fail to apply an approach with a sound phenomenological basis. Energy balance designs (5) remain inadequate because they require a prior knowledge of the operating efficiency, which is seldom available. Advances in multiphase flow theory have permitted design by an accurate momentum balance, as described below.

APPROACH

Pressure requirements

For a particular application, the required lift and volume flowrate of liquid are generally specified, and the air pressure and flowrate requirement must be predicted to size the compressor or blower. Air pressure is simply determined by calculating the hydrostatic head of liquid at the proposed point of air introduction, usually near the bottom of the pump and adding this to the absolute pressure in the feed tank, P_1 . Referring to figure 1, this pressure is given by the equation

$$P_0 = \rho_L g(x_1 - x_0) + P_1 \quad 1$$

where ρ_L is the fluid density. All calculations for air lift pumps should be conducted using absolute pressures.

Momentum balance

Volume flowrate of air is not as readily predicted, and must be found by performing a momentum balance over the length of the pump. The difference in pressure over the length of the pump, $P_0 - P_2$, at equilibrium must equal the sum of the hydrostatic head in the pump, pressure change due to acceleration of the fluid, and frictional losses at the pipe wall. For the simplest case, where the tank and header pot are at atmospheric pressure,

$$P_0 - P_2 = \rho_L g(x_1 - x_0) \quad 2$$

Neglecting the small contribution of the air in the pump, the hydrostatic head is given by

$$\Delta P_H = \rho_L(1-\epsilon)(x_2-x_0)$$

3

where ϵ is the void fraction of air present in the pump. The air void fraction is smaller than the ratio of air flowrate to total flowrate for two reasons. Firstly, the air is present in large bubbles or slugs which are axially situated, and which are separated from the pipe wall by a film of liquid. These slugs are therefore more concentrated near the pipe center, where the flow velocity is higher, so that this "profile effect" serves to reduce the air void fraction. Secondly, the air slugs rise relative to the liquid, which flows back around the slug in the annular film, so that there is a local slip effect which further increases the gas velocity. Both of these effects are accurately modelled by a drift-flux analysis (1,6,7,8), which predicts the gas void fraction, ϵ , by the equation

$$W_G/\epsilon = C_0(W_L+W_G)+V_v$$

4

where W_G and W_L are the gas and liquid superficial velocities, C_0 is a constant accounting for the profile effect, generally 1.2 in turbulent flow (1,2,6) and V_v is the drift velocity accounting for local slip, given by the equation

$$V_v = 0.35(gD)^{0.5}$$

5

where D is pipe diameter, for low viscosity liquids. Compensation for high viscosities is discussed by Govier & Aziz (3). Since the pressure changes over the height of the pump, the gas superficial velocity is not constant throughout the device. As an accurate approximation for short pumps, the gas superficial velocity, W_G , used in equation [4], is evaluated at the mean pressure in the pump

$$W_G = Q'_G P' / A(0.5P_2 + 0.5P_0)$$

6

where Q'_G is the free air volumetric flowrate, P' is atmospheric pressure, and A is the pipe cross sectional area.

Frictional losses can be evaluated by assuming that there are no losses at the wall from the annular film surrounding an air slug, and that all losses occur in the liquid zone, which is in contact with a fraction of approximately $(1-\epsilon)$ of the pipe wall. Since, by continuity arguments, the liquid zone must on average travel at the total superficial velocity, W_G+W_L , the frictional losses, by analogy with single phase turbulent flow, are

$$\Delta P_F = f \rho_L (x_2 - x_0) (W_L + W_G)^2 (1 - \epsilon) / D$$

7

where the friction factor f is found from a conventional single phase diagram, using the Reynolds number,

$$Re = \rho_L (W_G + W_L) D / \mu_L$$

8

and ϵ is evaluated using equation [4].

An additional pressure term arises due to the acceleration of the liquid from a standstill at the base of the pump, to a velocity equal to the total superficial velocity at the top of the pump. At the top of the pump all of this liquid momentum is irreversibly lost. Upon entrance into the pipe, the pressure change due to momentum increase must be

$$\Delta P_{A1} = 0.5 \rho_L (W_L)^2$$

9

and pressure loss due to

acceleration from the point of air introduction to the top of the pump is given by

$$\Delta P_{A2} = \rho_L W_L W_{G2} \quad 10$$

where W_{G2} is the air superficial velocity at the top of the pump, given by

$$W_{G2} = Q'G/P_2$$

$$= W_G(0.5P_2 + 0.5P_0)/P_2 \quad 11$$

Although there are some additional irreversible losses as the liquid enters the base of the pump, these are small and can be neglected. Thus the total momentum balance over the pump is given by

$$P_0 - P_2 = \Delta P_H + \Delta P_F + \Delta P_{A1} + \Delta P_{A2} \quad 12$$

where the terms on the right hand side are given by equations [3], [7], [9] and [10] respectively. Equation [12] must be satisfied to predict the free air flowrate, $Q'G$, required to produce a given liquid superficial velocity, W_L , in the pipe. In practice this can be done by rearranging the relevant equations into a simpler solution (9), or by writing a short computer program, and finding $Q'G$ by trial and error, which is still a very rapid procedure. As few as six points determined in this way will define an operating curve quite accurately.

PROBLEMS ENCOUNTERED

The case of a tall pump

The equation developed above is for the case of a short pump, because an average air superficial velocity has been assumed in

developing all of the equations. The air superficial velocity changes in a non-linear fashion over the pump length, so that this assumption causes overprediction of the required air flowrate when applied to very tall pumps. However, Dabolt & Clark (10) have demonstrated recently that the short design approach is quite accurate for typical pumps up to 30 meters in height, when compared to a more complex tall pump momentum balance (2,11). Thus the design approach presented above should be sufficiently accurate for most toxic and radioactive liquid pumping installations.

Practical design problems

Although the momentum balance solves the problem of relating the air and liquid velocities in the pump, there are some practical problems to the pump design which must be discussed. Firstly, the air must be introduced into the pump a short distance up the pipe, otherwise there is the danger that the air will bubble back into the tank, so that the air lift pumps at a reduced rate or not at all. Secondly, the mixture leaving the top of the tube must be separated into air and liquid streams. Although fairly sophisticated header pot designs have been proposed for this purpose (4), invariably some liquid droplets are entrained in the exit air, and some air leaves as bubbles in the liquid stream. Provision for this problem must be made, because the contaminated air cannot be discharged immediately to atmosphere. In addition, the air lift pump must be supplied with sufficient submergence to operate effectively: the strong effect that submergence has on flowrate is

discussed in the section below.

RESULTS

The validity of a momentum balance design approach has been demonstrated previously by comparison with data from air lifts ranging from 6 to 250 meters in height (1,2,9,11). In this paper, the momentum balance will be used to demonstrate the strong effect of submergence on the air lift operating curves. Figure 2 presents operating curves for a pump 10 meters in height and 100 millimeters in diameter lifting water at submergences of 3.5, 5 and 7 meters, using a typical friction factor of

0.01. Both the tank and header pot were taken as being at atmospheric pressure. The submergence has a very strong effect on the maximum flowrate which can be expected from the pump, and also on the air rate required to lift the volume of water. At very low submergences the pump will be incapable of lifting any liquid.

Where the efficiency of the pump is given by (1)

$$\eta = \rho_L g W_L (x_2 - x_1) / [P_2 W_{G2} \ln(P_0/P_2)] \quad 13$$

figure 2 also demonstrates that pumps with a very low submergence are less energy efficient. Nicklin

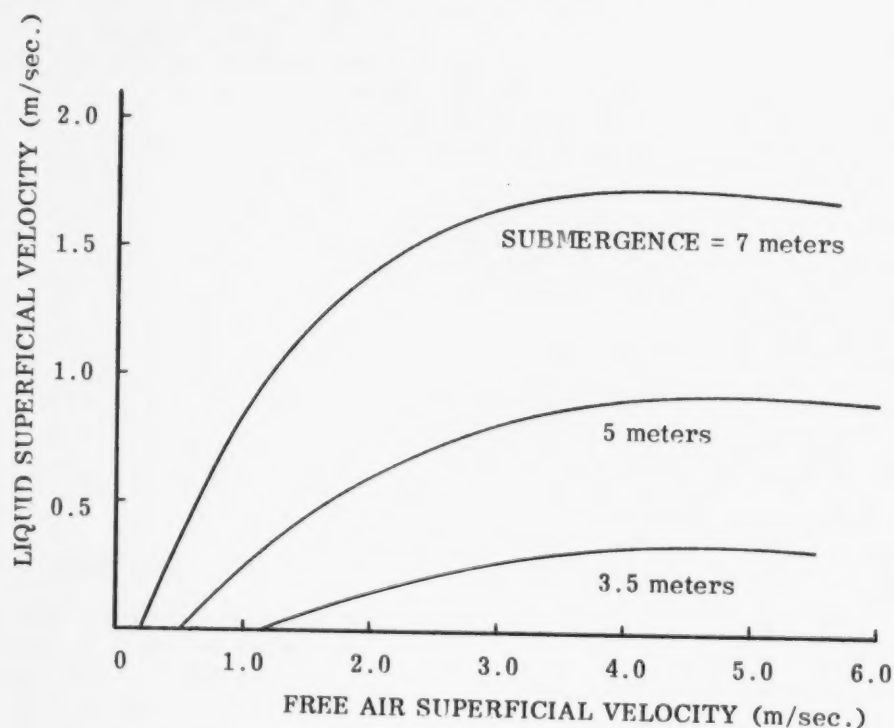


Figure 2: Operating curves for an air lift of 10 meters height at three different submergences. Friction factor = 0.01, Diameter = 100 mm.

(1) has shown that there is an optimum submergence for an air lift. Except in cases where there are specific limitations on the submergence available, a depth of 50 to 60% of the overall pump length proves most practical, although far lower and higher submergences have been used in practice.

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GREATER-CONFINEMENT DISPOSAL OF LOW-LEVEL RADIOACTIVE WASTES

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ABSTRACT

Low-level radioactive wastes include a broad spectrum of wastes that have different radionuclide concentrations, half-lives, and physical and chemical properties. Standard shallow-land burial practice can provide adequate protection of public health and safety for most low-level wastes, but a small volume fraction (~1%) containing most of the activity inventory (~90%) requires specific measures known as "greater-confinement disposal" (GCD). Different site characteristics and different waste characteristics--such as high radionuclide concentrations, long radionuclide half-lives, high radionuclide mobility, and physical or chemical characteristics that present exceptional hazards--lead to different GCD facility design requirements. Facility design alternatives considered for GCD include the augered shaft, deep trench, engineered structure, hydrofracture, improved waste form, and high-integrity container. Selection of an appropriate design must also consider the interplay between basic risk limits for protection of public health and safety, performance characteristics and objectives, costs, waste-acceptance criteria, waste characteristics, and site characteristics. This paper presents an overview of the factors that must be considered in planning the application of methods proposed for providing greater confinement of low-level wastes.

INTRODUCTION

Low-level radioactive wastes include a broad spectrum of wastes that have different radionuclide concentrations, half-lives, and physical and chemical properties. These wastes range from wastes containing naturally occurring radionuclides to mixed wastes containing both radioactive and chemical contaminants. Standard shallow-land burial (SLB) and other near-surface stabilization methods are most commonly used for disposal of these wastes. In a typical SLB facility, the waste is buried in shallow trenches about 8 meters in depth. Wastes containing long-lived, naturally occurring radioisotopes have, in many cases, been temporarily stabilized by simple means such as confinement in pits or covering with soil.

A small fraction of low-level wastes from both U.S. Department of Energy (DOE) and commercial sources contains radionuclides in sufficiently high concentrations

or with sufficiently long half-lives to require greater-confinement disposal (GCD), defined as "a technique for disposal of waste that uses natural and/or engineered barriers which provide a degree of isolation greater than that of shallow land burial but possibly less than that of a geologic repository" (DOE Order 5820.2).

In anticipation of the need for new land disposal facilities to better accommodate low-level wastes generated by DOE/defense and commercial activities, a Low-Level Waste Management Program was established within DOE to initiate and coordinate research and development activities for safe and cost-effective means for disposal of low-level wastes. The types of wastes that are being considered for GCD include: (1) wastes with high concentrations of short-lived radionuclides; (2) wastes with long-lived radionuclides; and (3) wastes co-contaminated with hazardous chemicals or chemicals that increase the mobility of radionuclides.

Wastes of the first type include some of the wastes generated by DOE and other government agencies as a result of defense activities, uranium-enrichment activities, and research and development activities as well as some of the wastes generated in commercial activities such as nuclear power production, manufacturing, medical applications, and research. Wastes of the second type are largely those containing naturally occurring radionuclides--e.g., mill tailings or raffinates, equipment, contaminated soils, and decommissioning rubble that remain at sites that were used for processing or storage of uranium and thorium ores and compounds.

The major reason that GCD is being considered for these types of wastes is the potentially unacceptable risks associated with releases to the environment and with human intrusion into the wastes if government control of the disposal sites were to cease in the future. Possible reasons for cessation of control are loss of funds and catastrophic events.

The methods for greater confinement can be grouped according to modifications to the disposal cell or modifications to the wastes or packaging. (The term "cell" is a general term indicating an individual hole, trench, shaft, or structure in which wastes are emplaced for disposal.) Modifications to the disposal cell include augered shaft, deep trench, and engineered structure. The special disposal technique of hydrofracture is also being considered as an example of greater confinement. Modifications to the wastes and packaging are commonly referred to as improved waste form and high-integrity container (HIC), respectively.

PURPOSE

The purpose is to present an overview of the factors that must be considered in planning the application of methods proposed for providing greater confinement of low-level wastes, to present methods for evaluating existing and conceptual disposal units that would provide greater confinement of low-level wastes, and to review the characteristics of a limited set of designs that have emerged from these several efforts as the most promising for providing the confinement that may be required for these waste types.

APPROACH

The characteristics and expected volumes of wastes that might require greater confinement were derived from data bases that have been collected by DOE contractors. In general, these wastes could not be disposed by technologies referred to in 10 CFR 61 regulations. Greater confinement for even larger volumes than these is being requested by some citizen groups despite the fact that the characteristics of the wastes might permit less sophisticated and less costly disposal technologies. Current regulations on low-level wastes are purposefully not prescriptive with respect to technology; however, they do refer to SLB but not to any of the designs discussed here. Criteria expressed by the International Commission on Radiological Protection (9) are used in this work as minimum indications of the performance objectives that greater confinement must achieve. The possibility is explored of expressing performance assessment, i.e., analysis of the behavior of the technology and its compliance with performance objectives, in terms of risk analysis. The role of cost and benefit in selection of disposal technology by potential operators is also considered. Several design options were selected for this assessment, and these options are examined to identify the basic elements in each option that will support the performance objectives. The advantages and disadvantages associated with each option are also discussed.

PROBLEMS ENCOUNTERED

One problem encountered in this work was the brevity of information available for some disposal unit concepts, especially the engineered structures. The expected performance of some disposal unit alternatives was difficult to evaluate because of the incomplete state of development of some of the concepts. Regulations on low-level waste disposal such as 10 CFR 61 and DOE Order 5820.2 are not restricted to SLB; for example, the U.S. Nuclear Regulatory Commission (NRC) maintains that it could assess the licensability of alternative disposal units by the 10 CFR 61 guidelines. Nevertheless, these regulations--although only recently finalized--were developed before the even more recent surge of interest in alternatives to SLB.

Performance assessment of GCD by the methods of risk analysis and cost-benefit criteria could not be carried to the point of quantitative results because of the lack of parameters needed as input to the calculations.

RESULTS

Waste Characteristics

The expected characteristics of wastes--especially their radiological, chemical, and physical properties--will be the most important determinants not only of whether GCD is required but also of which GCD technique will be applicable for a given disposal site. The concentration of radionuclides in the low-level wastes will be the primary index of whether they must be managed by GCD techniques. For commercial wastes, it is expected that any wastes exceeding the Class C radioactivity concentrations defined by 10 CFR 61 will require management by GCD, but site-specific criteria may also require that wastes of concentrations lower than the limits of 10 CFR 61 be treated by GCD. For example, at the Savannah River Plant, some wastes that do not exceed concentrations corresponding to the limits of Classes C, B, or even A are managed by GCD techniques.

Our knowledge of the characteristics, volumes, and properties of wastes in the United States that will require disposal is continually being improved by several waste inventory systems (11). The annual review by DOE (20) also presents information on U.S. waste inventories that will aid decisions on which wastes are likely to require GCD. Current estimates indicate that about 1% or 1,600 m³/yr (2,100 yd³/yr) of all low-level wastes may require this special treatment (7,20). In addition, a total of 2.3×10^7 m³ (3×10^7 yd³) of materials contaminated with long-lived, naturally occurring radionuclides awaits permanent disposal.

Regulations

Regulations specifically for management of GCD wastes have not been expressed in detail, but general guidelines are given in DOE Order 5820.2, 10 CFR 61 (NRC), and the criteria, rules, and laws being developed in the formation of state compacts. The policies of DOE Order 5820.2,

Chapter III, that apply to wastes generated at DOE-controlled sites give general guidelines for the waste-acceptance criteria that must be developed by each DOE disposal site. The criteria of 10 CFR 61, which apply to commercial wastes, indicate the limits above which wastes require greater confinement than conventional SLB. Although the regulation of GCD has not been explicitly defined, at least the concentrations of radionuclides at the site boundaries of a facility are defined by the concentration limits of 10 CFR 20; DOE Order 5480.1A, Chapter XI; and the drinking water limits of 40 CFR 141. These represent goals for performance of GCD techniques. The 10 CFR 61 regulations indicate that more specific guidance for alternatives to near-surface disposal of low-level wastes, e.g., 10 CFR 61.50(b) on site selection, will be developed. In addition to these regulations and criteria, plans for design and construction of a GCD facility may require an environmental evaluation in compliance with the National Environmental Policy Act of 1969.

Each GCD alternative carries with it certain waste-acceptance restrictions and thus imposes some restrictions on waste generators. Although the site-selection criteria for application of improved waste form or HIC may not differ from those for SLB, there will be additional criteria relative to the GCD techniques of deep trenches, engineered structures, augered holes, and hydrofracture--of which some criteria will be unique to each method.

Performance Assessment

The importance of assessing the technical performance of a disposal facility--before, during, and after its operational lifetime--is emphasized in 10 CFR 61 and DOE Order 5820.2, and it is likely that performance assessment of a GCD system will also be treated with importance. The performance of a disposal facility is customarily assessed against performance objectives. Although federal regulations (10 CFR 61, 10 CFR 20, and DOE Order 5480.1A) imply performance objectives and although each regional compact is expected to express its own set of objectives, the clearest current statement of performance objectives is presented in the basic rules of the International Commission on Radiological Protection (9). The essence of

these rules is that risk to both the general public and occupational workers should be limited. The basic dose limits are 500 mrem/yr for short-term exposure and 100 mrem/yr for lifetime exposure. The occupational limits are greater by a factor of 10. Decisions among design alternatives should be based on (a) the expected technical performance that will permit achievement of these performance objectives, and (b) the cost of achieving a given level of technical performance. Thus, ideally, the choice of disposal techniques should be made on the basis of benefit-cost-risk (BCR) analysis. The application of this type of assessment to GCD techniques has been described by Gilbert and Luner (7).

Planners and waste generators anticipate that the cost of GCD will be greater than the cost of SLB. Based on some cost estimates for GCD designs that have been made (7), costs are expected to increase in the order SLB < deep trench or SLB with intruder barrier < augered shaft < concrete-walled trench < improved waste form. Costs are strongly dependent on site characteristics; hence, site-specific considerations could alter this order. Hydrofracture is too dependent on site-specific factors to permit inclusion in this ranking. If geologic conditions permit the use of hydrofracture, it is probably the most cost-effective disposal method for liquid waste and a comparable disposal method for solid wastes that can readily be formed into a slurry (e.g., ash from incinerated low-level wastes). The cost categories in which GCD is expected to differ significantly from SLB are labor, materials, post-operational stabilization, and purchase and replacement of equipment.

Although a BCR analysis can be mathematically expressed, the lack of parameters with which to obtain quantitative results has led to the proposal to make decisions among GCD alternatives by a two-part assessment method: (1) quantitative estimation of risk associated with a disposal method by modeling the migration of radionuclides from the disposal site (pathway analysis), and (2) qualitative comparison of the attributes of alternative disposal techniques. The results of calculating the concentrations of radionuclides at various distances in pathways leading from a disposal cell can

be used to compare the risks associated with alternative designs. The qualitative comparison of technical performance can be based on an evaluation of the contribution to realizing the performance objectives that would be made by performance attributes such as the characteristics of the waste form, container, design of the disposal cell, emplacement procedures, and emplacement equipment. The assessment can be carried into further detail by determining which designs provide the even more basic elements that are ultimately responsible for those performance attributes: intrusion resistance, compressive strength, corrosion resistance, radiation stability, drainage control, infiltration resistance, leach resistance, biodegradation resistance, ion-exchange capacity, thermal stability, distance from surface, distance from hydrologic movement, permeation resistance, distance from radiation sources, minimum time of exposure to radiation sources, shielding, structural stability, and chemical inertness.

Disposal Cell Design Alternatives

A few disposal cell concepts have been considered to be practicable by several evaluations. These concepts are being catalogued in an overview of GCD, currently in preparation, that will be published as one of the DOE handbooks on management of low-level wastes. These concepts include augered shaft, deep trench, and engineered structures.

The augered shaft consists of a hole in the ground with a diameter of 3 to 4 m and a depth of 10 to 35 m, as exemplified by demonstrations at the Nevada Test Site (13) and the Savannah River Plant (14). Smaller, shallower boreholes have been used for waste disposal in the United States and other parts of the world. The advantages of the augered shaft include a geometry that shields operators from emplaced radioactivity; compatibility with remote-handling techniques; remoteness from plant and animal intrusion; easy closure, both temporary and final; and low susceptibility to erosion. A disadvantage of the augered shaft is the limited size of the waste items that are acceptable to the typical diameters of the shafts.

The deep trench disposal unit is an excavation that is deeper than the normal

8-m depth of the SLB trench. The wastes are surrounded with soil material in the deep trench, as in SLB. The deep trench has not received much attention either in design or in use. One of the earliest references to the concept suggested that it would be quite similar to an SLB unit except twice the depth of a conventional SLB (10). In addition to the advantage of placing wastes beyond the depth of penetration of roots and animals, the deep trench offers simplicity, flexibility in acceptance of waste types, and little vulnerability to erosion. The deep trench, however, requires a site that has an unusually thick layer of soil and unconsolidated materials over the water table. Furthermore, unless special shoring techniques are used, the wide opening required to excavate a deep trench will involve a relatively large area and may restrict emplacement techniques to unloading a waste-carrying vehicle at the bottom of the trench.

The engineered structure is a disposal cell in which one of the most important barriers to intrusion and release of radionuclides is a chamber typically built of concrete. A large variety of designs have been described, involving placement of wastes both above and below grade level (2,8). These include the Canadian concrete-walled trench (5), the Savannah River Plant concrete-shored trench (14), the French tumulus (24), the NRC concrete-walled trench (21), and the concrete chamber of the University of Arizona (25). The main advantage of engineered structures is their potential barriers to infiltration and intrusion. Structures that are initially roofed will also provide protection from adverse weather during emplacement operations. However, because concrete is prone to eventual cracking, the engineered structure eliminates neither infiltration of water nor release of leachate over the long term. Recently, a preference for engineered, above-grade disposal units has been expressed in planning facilities that will be operated by state governments for disposal of low-level waste (23). Above-grade structures have received considerable attention because they are perceived to offer advantages for protection from groundwater and also for ease of surveillance, maintenance, and remedial action.

Hydrofracture for Greater Confinement

The waste-emplacement configuration of the hydrofracture alternative consists of a stack, several hundred meters in diameter, of thin sheets of grout incorporating the wastes; the grout sheets are interleaved between underground shale layers. This unique waste-emplacement configuration sets hydrofracture apart from the category of disposal cells discussed in the foregoing sections. Disposal by hydrofracture (mixing wastes in liquid or slurry form with cement and injecting the mixture into horizontal fractures in rock formations located several hundreds of meters below the earth's surface) has been practiced successfully over a period of many years at Oak Ridge National Laboratory (26). The advantages of hydrofracture include a high degree of isolation from the environment and from intruders, a small commitment of surface land area above the disposal zone, and a relative insensitivity to weather during emplacement and to erosion after emplacement. The disadvantages of hydrofracture include applicability only to wastes in liquid or slurry forms or to wastes that can be converted to such forms, the possible stimulation of minor seismic effects, and the requirement that the disposal site have special geologic characteristics. Also, if contamination of deep aquifers did occur, remedial action would not be feasible.

Improved Waste Forms for Greater Confinement

Whereas the GCD technologies described in the foregoing sections have emphasized confinement by geologic media, the concept of improved waste form emphasizes the capability of confinement derived from the physical and chemical properties of the waste form. Improved waste forms are generally solid media into which primary waste forms are incorporated. Among the advantages of improved waste forms is the potential for their use in an ordinary SLB trench to provide GCD. Also, they provide some attenuation of penetrating radiation, are independent of site characteristics, permit retrievability in case of need for remedial actions, limit dispersion in case of accidents, and reduce migration of radionuclides caused by leaching. Among

the disadvantages of improved waste forms is the involvement with chemical processing equipment--with the attendant needs for maintenance, decommissioning of contaminated equipment, and costs. Some solidification agents are unable to completely incorporate all waste forms, particularly oils and organic liquids. The solidification agents used to produce improved waste forms can be grouped into three types: cement, organic solids, and glass (6,15). Cement is the most commonly used solidification agent in management of radioactive low-level wastes. Additives such as organic polymers, silicates, and gypsum improve such properties as ability to incorporate oils, mechanical strength, and leach resistance; they introduce, however, some chemical-processing complications. Some organic solidification agents that have been investigated and used to varying degrees in actual practice are urea-formaldehyde, bitumen, epoxy resins, and vinyl ester-styrene. Urea-formaldehyde, once widely used, has now been rejected, mainly because of its release of contaminated water; bitumen, used frequently in Europe, but infrequently in the United States, still seems acceptable for some applications; epoxy resins are offered in commercial waste-solidification systems; and a vinyl ester-styrene process is available in another commercial solidification system. Although glass waste forms have been developed mainly with the intention of application to high-level waste, their application to other wastes also seems feasible according to a recent evaluation (1).

High-Integrity Containers for Greater Confinement

Another GCD technique that relies on factors other than those of geologic media to provide confinement is the high-integrity container (HIC). Its confinement capabilities are based on its design and on the physical and chemical properties of the material from which it is fabricated. A high-integrity container is a vessel that is intended to provide structural stability and containment of radionuclides for a long period; characteristics of the HIC have been more specifically defined in criteria formulated by regulatory bodies such as the NRC and the state of South Carolina (4). Designs of containers intended to meet criteria for HICs have been developed by several organizations

(3,12,16,27). The favored materials of construction are polyethylene and concrete. Sizes vary from 55-gal drums to large units that can be handled only by powered cranes. In many cases, emplacement of an HIC in an ordinary SLB trench should provide the security required for GCD without the cost or trouble of constructing any more sophisticated disposal unit. Probably the most serious disadvantage of the HIC is its inability to accept large items, e.g., those that may occur occasionally as a result of decommissioning activities such as vehicles, cranes, processing equipment, and rubble from the demolition of buildings.

Confinement of Low-Level, Long-Lived Wastes

Because the radioactive constituents of long-lived wastes--raffinates, tailings, rubble, and contaminated soil material--are mostly isotopes of uranium and thorium with their daughters, a major concern is the control of radon release. Thus, a diffusion barrier that slows the escape of radon to permit most of it to decay before reaching the atmosphere--consisting of a medium of low permeability, e.g., clay--is common to most designs of disposal units for this type of waste. Such a barrier can do triple duty if it also has the capacities to slow the migration of ionic radionuclides, as some clays do, and to resist the infiltration of water. Designs for these disposal units place the wastes either above or below the earth's surface. Design criteria for such disposal units include multilayered caps of natural materials that provide--with little maintenance--drainage, physical stability, erosion resistance, and intrusion resistance. Examples of the latest designs for such units are given in plans for handling wastes at West Chicago (22), Weldon Spring (18), Niagara Falls (19), and Cannonsburg, Pennsylvania (17). More recently, however, groups concerned with safe disposal of wastes are demanding that design elements similar to those of engineered structures be evaluated for confining these types of wastes, including man-made materials for drainage and resistance to water infiltration. The augered shaft technology might be applicable to this type of waste, but it might not satisfy the current preference of citizen action groups and state planners for above-grade emplacement of wastes.

Conclusions

The need for disposal technology offering greater confinement than SLB arises not only from the existence of wastes exceeding the regulatory limits for SLB, but also from individual policies of organizations and demands of concerned citizens. The number and variety of technologies judged capable of providing greater confinement than SLB have been expanded. Several of them that have been perceived to be technically feasible and applicable to the types of wastes for which greater confinement is being demanded have been briefly described and evaluated here. Applicability of any one of these techniques to an individual disposal problem will depend on the characteristics of the wastes and the disposal site. It is expected that not only the selection of the technology to be applied but also the need for GCD will have to be established on a case-specific basis.

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DESIGN OF RADIOACTIVE TAILINGS DISPOSAL
SITES TO LAST 1,000 YEARS

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ABSTRACT

Cleanup and stabilization is currently being conducted by the Department of Energy at 24 inactive uranium mill sites involving from 100,000 to more than 3,000,000 cubic yards of radioactive tailings and other contaminated materials. The applicable EPA standards provide standards for radiation control and stress the use of passive controls such as thick, earthen covers, below ground disposal or rock covers to achieve a minimum maintenance free design life of 200 years and, ideally, 1,000 years.

The 24 mill sites in question are principally in the semi-arid areas of the Western USA. The majority were built on the banks of or very close to rivers so most of the tailings piles are in floodplains and vulnerable to flood erosion. Another common problem is ground-water contamination. Since most ponds were not lined, large quantities of the tailings water percolated into the ground and contaminated the near surface aquifers with uranium, selenium, arsenic, sulfates, and similar toxicants.

These conditions, along with the radioactivity required that the design consider radiation reduction, prevention of wind or water erosion, protection from catastrophic events and minimization of water infiltration into the stabilized tailings.

This paper discusses the selection of design criteria sufficiently conservative to assure a high probability that the embankment will last 1,000 years or more essentially intact. Among the criteria utilized in the designs are the application of Maximum Credible Earthquake, Probable Maximum Precipitation and Probable Maximum Flood to the location, and configuration of the proposed disposal site.

INTRODUCTION AND PURPOSE

Title I of the Uranium Mill Tailings Radiation Control Act of 1978 authorizes the Department of Energy (DOE) to cleanup and isolate from the environment the radioactive tailings and other contaminated materials at 24 inactive uranium mill sites. The principal purpose of this act is protect the public health from the radionuclides that are either emitted from the tailings as radon gas or carried away from the sites by wind or water movement.

The U.S. Environmental Protection Agency (EPA) established health and environmental standards to govern the cleanup and control of these radioactive materials in 1983. In developing the standards, EPA determined "that the primary objective for control of tailings should be isolation and stabilization to prevent their misuse by man and dispersal by natural forces such as wind, rain and flood waters. Consequently, the

standards set forth the following design objectives:

- Reduction of the radiation emissions (in the form of radon gas) to less than 20 pCi/m²
- Effective isolation of the tailings from the environment for at minimum of 200 and ideally 1,000 years
- A "maintenance free" design

As prime contractor to DOE, the first priority of Jacobs Engineering was to establish design criteria and an approach that fulfilled the standards and objectives and was acceptable to the Nuclear Regulatory Commission (NRC), EPA and States.

The design of any engineered system to meet a maintenance free design life of 200 to 1,000 years is complicated from the start by the absence of any historical (or empirical) examples. The more famous historical engineered systems in the range of 200 - 1,000 years old - forts, castles, earthworks, canals, irrigation systems, etc. all either show the effects of wind/water erosion or require constant care. Further, research and development of engineered systems to withstand the vagaries of nature is relatively new activity with only 50 to 100 years of data and observations. Finally, the record of the major natural forces, wind velocities, rainfall intensities and duration, flood velocities and depths, etc. only cover about 70-80 years maximum in most of the localities and the measuring stations usually are not very near to the site(s) being evaluated. Consequently, the selection of 200-1,000 year design criteria involves coupling scientific data, statistical methods and an evaluation of risk.

APPROACH

Developing design criteria to meet the first of the objectives, radiation protection, was relatively easy. Through research sponsored by

DOE, NRC and others, radiation reduction was demonstrated to be effectively achieved by the use of a soil cover system to trap the radon gas until it decayed to solid radionuclides. This system ranged from approximately 1-1/2 to 3 meters thick depending upon several factors including the strength of the radioactivity (source term), types of soils available for cover materials (sandy/silty clays attenuate radon better than sands or silts), the expected long-term moisture content and the degree of compaction.

Protection of the radiation barrier or soil cover system required much more extensive engineering analysis. The most critical design concerns include differential settlement which could rupture the cover system, slope failure which could also result in the exposure of tailings, prevention of erosion from both normal weather events and large, intensive rainfalls and the associated runoff. Coupled with the concern about embankment erosions is the related concern about regional erosion potential (gully formation, etc.) and river channel migration. Finally, protection of ground-water requires an analysis of the impacts of ground water movements up into and through the pile, the effects of the cover system on ground water and the transitional impacts of construction water on ground-water quality. These can be summarized as four principal design concerns:

- Stability
- Longevity
- Ground-water protection
- Cost

The stability design criteria were also not too difficult to establish. Since the tailings piles had random sand and slime layers, wedges and/or deposits, it was recognized quickly that design criteria were required for slope stability and differential settlement.

Most of the tailings piles presently exist at or near their natural angle of repose - someplace between 1.5 and 2.0 horizontal to 1.0 vertical. These steep slopes are very susceptible to slumps,

slides and erosion. Drawing upon previous work by DOE and NRC (DOE-1), a design criterion of maximum side slopes of 5H:IV was established. Further, the stability of this slope was verified by establishing the worst case pile profile (thickness and number of sand/slime layers plus cover system) and calculating the passive factor of safety and, using the maximum credible earthquake to determine the dynamic factor of safety.

Differential settlement would be minimized by homogenizing any relocated tailings and by compacting both the tailings and the cover system to at least 95% dry density.

The factors which affect the long-evity and their associated effects including:

- * water/wind erosion - cover damage
- * regional erosion potential - gully ing and under cutting
- * flooding - catastrophic embankment failure
- * river erosion/migration - undercutting and erosion of embankment systems were more difficult to develop acceptable design criteria for.

The effects of water/wind erosion are related to the exposed surface materials and the exerted erosive forces. The selection of surface materials is principally dependent upon the areal climate. Since most of the sites are located in semi-arid areas, it was immediately recognized that a vegetated cover could not be established and maintained without some form of irrigation system which defeated the maintenance-free objective. Therefore, a rock or gravel cover layer was incorporated into the design to withstand the wind and water erosive forces.

The design wind/water erosive forces are dependent on the magnitude of the selected design event. Further, the erosive forces of an intense rainfall are

recognized as far exceeding those from any windstorm so it was decided that design of an erosion protection layer for runoff would protect equally well against the wind. (DOE-2)

Since the ideal design life is 1000 years, it was obvious that the wind velocity or rainfall intensity had to be at least equal to that generated by a storm with a recurrence interval of 1000 years or more. However, since these are random events, there is some probability that an even larger event will occur within 1000 years. This probability (or risk) can be calculated for any larger event (500 year, 1000 year, etc.), but there are two complicating factors. First, there is a large degree of uncertainty in extrapolating 50-100 years of historical meteorological records to larger storms with more infrequent recurrence intervals. Second, there is no established or agreed on "reasonable" risk (i.e., 10%, 1%, 0.1% chance of a larger than design event occurring and breaching the embankment) to be used in the design. Therefore, design methods must be adopted which incorporate conservatism into the design. The design criteria for the stability of the UMTRA Project tailings piles due to erosive forces resulting from rainfall runoff across the top and down the sides of the stabilized embankment are based on the runoff from the localized Probable Maximum Precipitation (PMP). The PMP is the worst possible event that could occur as a result of a combination of the most severe meteorological conditions occurring over a watershed at the same time. Although no recurrence interval can be assigned to this event, it is felt by most experts that the recurrence interval is in excess of 100,000 years. This roughly equates to a less than 1% chance that a PMP event will occur in the next 1000 years. Procedures investigated for calculating the required mean rock size needed to provide a stable rock slope during the PMP included:

- * Bureau of Public Roads (Searcy, 1967).
- * U.S. Army Corps of Engineers Waterways Experiment Station U.S. Army, (1970).

- ° California Division of Highways (Cal. DPW, 1970).
- ° ASCE Task Committee on Preparation of Sedimentation Manual (ASCE, 1972).
- ° Bureau of Reclamation (Bur. Rec., 1958).
- ° Lane's Method (Lane).
- ° Campbell's Method (U.S. Army, 1966).
- ° Wyoming State Highway Department (Safety Factors Method) (Stevens, 1976).
- ° Rockfill in Hydrologic Engineering (Stephenson, 1979).

All of these procedures use one of four basic approaches:

- 1) critical velocity, 2) lift and drag force mechanisms, 3) critical shear stress, or 4) empirical solutions.

The critical velocity equations consider the impact of flowing water on the particles such that the material of a given size and weight is just able to move. Inherent in this approach is the lack of good definition of the bottom velocity and the difficulty in accurately measuring or predicting this velocity. Another difficulty in using this approach is determining the relationship between bottom velocity and average velocity.

The lift force mechanism approach accounts for a pressure differential caused by the gradient of the velocity. The pressure differences occur because of steep velocity gradient, where the velocity at the top surface of a particle at rest on a channel bottom is greater than zero, while the velocity at the bottom surface is zero. This method although important, has been difficult to develop. Additionally, the critical shear stress and critical velocity methods implicitly include the lift force effects.

The critical shear stress equations consider frictional drag of the flow on the particles and considers the fluid shear stress on a rock layer to the mean flow velocity. This approach is the best for the UMTRA project because mean cross-sectional velocities, depths and flow can be easily obtained assuming sheet flow characteristics.

The design method which is most applicable to the design of a rock blanket for erosion protection on the top and along the toe of the embankment is the "Riprap Design with Safety Factors Method" developed for the Wyoming State Highway Department by Stevens et al. (1976). The theory and formulation of this method are not discussed as part of this paper since they are well documented in the published paper. This method is based on the theory of critical shear stress and allows more flexibility in design because the designer is able to choose the factor of safety needed for the design of a particular site and work through the analysis to determine the required rock size. This flexibility is particularly important when considering the conservatism associated with using the PMP as the design storm.

Either the Safety Factors Method or the Stephenson Method, which is based on critical shear stress, are suited for the design of the rock layer on the side slopes for a PMP centered on the embankment. The Safety Factors Method is applicable so long as the depth of flow is greater than 0.5 times the mean rock diameter. Below this ratio, the Safety Factors Method is not accurate and the Stephenson Method must be used because the flow is no longer sheet flow but is interstitial among the rock particles.

The selection of a design flood event to achieve the EPA longevity requirement would appear to be straight-forward. The standard request from the Nuclear Regulatory Commission (NRC), and the standard design approach taken, is to determine the magnitude and potential

impacts resulting from a Probable Maximum Flood (PMF) event. However, the use of the PMF as the control of uranium tailings is not clear-cut.

The EPA standards do not specifically state that a PMF event must be used for design in order to achieve the stated containment life. An analysis of exceedence probabilities for various events with respect to the containment life (Junge and Dezman, 1983), suggests that design events with a very long return period (e.g., 10,000 years or greater) must be used to meet a longterm containment objective. However, the limited statistical record available cannot accurately be extrapolated to such long return periods. Therefore, the generally accepted alternative, by default, is to use maximum credible events such as the PMF for design purposes.

By definition, a PMF is based on the most severe combination of critical meteorologic and hydrologic conditions for a particular area, and has a very small chance of being exceeded. Therefore, a tailings disposal system designed to withstand a PMF would have a very small risk of failure and thus, meets both the intent and containment objective of the EPA standards.

Although the use of a PMF meets the intent of the EPA standards, this does not mean that designing for a flood of lesser magnitude would not also meet the longevity requirement. The use of a lesser flood event, however, is strongly discouraged by the NRC and concurrence would be difficult to obtain.

The simplest approach is to use the PMF as the design flood event but recognize that the conservative nature of its use is like having a built-in factor of safety. This fact can be used as the basis against having to apply additional arbitrary factors of safety and overly conservative parameters throughout the remainder of the design.

Developing the design velocities and depths related to the PMF was done using the HEC-1 and HEC-2 Models (COE, 1981, 1982). The principal inputs to the HEC-1 Model, which develops the hydrograph are:

- * PMF estimates and hydrographs for each distinct drainage area in the basin
- * Hydrograph time interval
- * Soil infiltration rate on runoff curve numbers
- * Lag times for each subbasin.

The PMF estimates are generally derived from the National Oceanic and Atmospheric Administration (NOAA) Hydromet publication appropriate to the area. Since most of the mill tailings sites are west of the 105° meridian, the hydrographs had to be developed and input directly.

Normally, flood hydrograph time intervals are chosen to be either 15 minutes or one hour. The 15 minute interval will produce a much higher peak flow than using a one-hour interval. It was concluded, however, that a time interval of less than one hour is too detailed for the magnitude of a PMF analysis.

Soil infiltration is more difficult to effectively estimate. Soil infiltration rates can be directly input into the HEC-1 model; or runoff curve numbers can be specified and used by the model to calculate the soil infiltration rates based on empirical formulas. Either method requires a knowledge of the soil and vegetation characteristics of the drainage basin. With small drainage basins, this evaluation can be easily accomplished. Unfortunately, most of the tailings sites located in or near flood plains are impacted by drainage basins comprising thousands of square miles. The parameters are highly sensitive and can vary the results by several hundred percent.

If runoff curve numbers are used, it should be noted that this system was originally developed solely for agricultural land. The basis upon which the empirical equations were developed is not well published nor understood. There is also a wide variation in curve numbers depending on what antecedent moisture condition (AMC) is used. Lower curve numbers are specified for an AMC-II condition than an AMC-III conditions (DOI, 1977). The user may feel in his judgement that an AMC-II condition is sufficient for use with a PMF. However, it is noted that the opinion of the NRC is to use an AMC-III condition.

It is the opinion of the design team that the method of specifying the soil infiltration rate is not only easier to develop but also has a more established basis. As an example, through discussions with the U.S. Army Corps of Engineers (COE) in Omaha, Nebraska, a map of "Soil Infiltration by Generalized Soil Groupings" (MBIAC, 1966) was obtained for use on the Riverton, Wyoming, site flood analysis. The COE has used it and recommended its use for PMF analysis. The NRC, on the other hand, has indicated that the recommended values on the map are too high. This is very important to note due to the extreme sensitivity of this parameter. A sensitivity analysis of this parameter on the Riverton site flood analysis showed that a 0.1 inch change in this parameter resulted in over a 200,000 cfs change in the PMF flow rate.

Lag times for subbasins throughout a watershed are typically computed using the lag time empirical relationship contained in Design of Small Dams (DOI, 1977). Experience has indicated that this relationship generally gives longer, less conservative lag times than what might occur. The approach of the design team is to initially calculate lag times with the above stated relationship. The resulting peak flows for each subbasin hydrograph are then used with Manning's equation to determine a better estimate of channel velocities. The velocities

are then used to recalculate the routing lag times.

Once the hydrograph was established, the flood routing was done using HEC-2 was relatively straightforward. The only serious concern was selecting appropriate Mannings "n" values for the channel and overbank areas.

The most difficult problem area to evaluate was the potential for river migration/realignment.

The primary geomorphic concern with long-term stabilization of sites located in flood plains is the potential for lateral movement of a stream channel causing undermining or erosion of the tailings impoundment. Stream channel migration can occur gradually during the period of containment. A more severe situation that can occur, however, is a rapid channel shift in response to a major flood event. The potential for channel migration must be carefully evaluated on a site - specific basis with all available geomorphic data. Two examples are given to illustrate the difficulty of correlating the possible geomorphic changes with the PMF analysis.

The Gunnison, Colorado site is a tailings pile located in a flat, terraced valley about 1 mile upstream of the confluence of the Gunnison River and Tomichi Creek. The entire valley was comprised of terrace gravels, sands and silts deposited by floods in prehistorical times and the difference in elevation between the site and the watercourses is only about 5 feet maximum, (Figure 1). The Rifle, Colorado site (Figure 2) is different in that the tailings piles lie in the modern floodplain about 1000 yards downstream of a 90° bend that is subject to continuous severe erosion forces.

In the case of the Gunnison site, the Gunnison River was classified as having only moderate with a high potential for channel migration. An evaluation of the existing Gunnison River channel alignment would indicate that during a PMF the alignment would shift laterally towards the site in a gradual

curve to the confluence with Tomichi Creek. A limitation of the HEC-2 model is that it cannot predict or estimate changes in channel configuration that might occur during a major flood event. Additional HEC-2 analysis was conducted to check mean channel velocities assuming that major erosion of the overbank area has occurred towards the embankment. The Gunnison River channel was assumed to have widened from its present location all to the edge of the embankment. The widened channel was assumed to have a uniform streambed elevation. Since the widened channel would have a uniform depth then the flow velocity at any point would equal the mean channel velocity. The resulting velocities and assumed depths of undercutting were then incorporated into the design to assure that adequate size and quantity of rock protection was provided at the top and sides of the embankment.

At the Rifle site, the Colorado River has a high potential for channel migration. The evaluation of the channel and floodplain topography showed that under PMF conditions the water would flow essentially from east to west across the site and the present pile alignment would be a large blocking force. To mitigate this, the proposed design specified realigning the tailings embankment on an east-west axis and pointing the upstream end like the prow of a ship. This, plus a riprap blanket extending from the embankment to the present dike were felt sufficient to prevent both undercutting due to daily erosive forces and breaching during catastrophic events.

PROBLEMS ENCOUNTERED

Interpretation and application of above design criteria were not without some problems in design conservatism. The reviewing agencies, in particular the NRC, wanted the safety factors (SF) to be calculated by both the circle of failure and sliding wedge approach even when the circle of failure showed SF's greater than 2.0. Also, there was a constant effort to design to higher SF's.

Commonly, a S.F. of 1.0 was used for all dynamic situations since it was argued that the low probability of the design events was in itself sufficiently conservative and the use of a higher S.F. was simply overdesign.

An additional problem was in amount of data required by the reviewing agency. It was standard practice to provide the regulators with design summaries and the supporting calculations and data. However, in almost all cases, the reviewing agencies, particularly the NRC, responded with requests for more data. At first it was justified in that the program was still being defined, but after the 4th site, it appeared that it may have been more the case of avoiding the decision by requesting "more study".

Finally, a part of the problem was the uncertainties in achieving a 1000 year design life. Since it had never been done before, even the methods were subject to a certain amount of reservation. It often appeared that personnel started out with a preconceived idea of rock size, PMF size, etc and then argued for the methods or assumptions that best supported their position. This made agreement on siting and design very difficult.

RESULTS

Notwithstanding the problems, the Jacobs design team were able to formulate an approach that was acceptable for the design of tailings embankments to last 1000 years. The basic approach was to first qualitatively analyze the potential for catastrophic failure - floods, earthquakes, etc. If this analysis indicated that the site was potentially stable, then a more detailed analysis was conducted.

Generally, the potential for flood damage or river channel migration were the most severe limitations and required the most engineering. Once this was done, a decision could be made on whether the tailings could be stabilized-in-place

or had to be relocated. Based upon this decision, the design of the final cover system proceeded without too much difficulty.

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Disclaimer

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A NOVEL TYPE OF NUCLEAR REACTOR - THE HYDRO REACTOR

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ABSTRACT

It consists of a solute uranium oxide in water. The nuclear fission induces four sorts of ionizing radiation. First the alpha particles from uranium self and the trans uranic nuclei such as plutonium or neptunium. Then beta particles issued from the fission products such as cesium and lanthanum. Third the fission neutrons that collide on H_2O molecules so as to eject secondary protons. At last the γ rays that ionize the H_2O molecules. These divide into a hydrogen and a hydroxide ion according to $H_2O \rightarrow H^+ + OH^-$. The hydrogen atoms react together in order to form H_2 molecules that rise out of the solution. The OH radicals react on heavy metal cations such as U^{4+} in order to form insoluble hydroxides that replace the H capture.

The reactor produces hydrogen as useful energy source and reduces the related radioactive waste in terms of its simplicity and life.

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EXTRACTION OF PESTICIDES FROM PROCESS STREAMS USING HIGH VOLATILITY SOLVENTS

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ABSTRACT

This cooperative agreement research program was initiated with the overall objective of determining the feasibility of extraction of pesticides from process waste streams using a liquid-liquid solvent extraction approach. A literature review provided foundational data in support of the technology identified for study through: (1) priority-ranking and selection of pesticides for project study and the identification of optimum solvents for liquid-liquid extraction, (2) compilation of various engineering design options for liquid-liquid extraction systems culminating in the selection of a design choice consisting of a counter-current-flow rotary disk contactor (RDC) process, and (3) application of literature on engineering design economics to formulate reliable cost estimates for the derived technology. While liquid-liquid solvent extraction is not new and has, in fact, been used in the chemical process industry for many years, it has seldom found use as a pollution control technology. The novel aspect of the technology described herein is that it uses volatile organic solvents (within a boiling range of 34°C - 78°C) with very low water solubility characteristics. The bench-scale RDC-type Solvent Extraction of Organic Pesticides (SEXOP) system was used to test both synthetic and real-world process effluent samples. Tests using the synthetic sample demonstrated extraction efficiencies in excess of 99.9 percent. Subsequent to process optimization, bench-scale runs using real-world process effluent samples (consisting of raw untreated waste) resulted in a clean-up for most constituents in excess of 99 percent. No constituents of the best-case raw untreated waste final run were extracted at an efficiency level below 90 percent.

INTRODUCTION AND PURPOSE

Research conducted on the project was structured such that the following three areas were addressed:

1. Solvent-pesticide partition coefficients were established through use of both synthetic pesticide mixtures and pesticide manufacturing wastewaters.
2. A bench-scale liquid-liquid extraction unit was designed and fabricated and experimental studies were conducted to test the capability of the system.

3. Subsequent to the bench-scale runs, economic feasibility studies were conducted in order to determine the potential process viability as compared to commercial-scale carbon adsorption systems.

Research objectives in the above three areas were met through work in the following four discrete task areas:

- Task 1 - Literature Review
- Task 2 - Screening Extraction Studies
- Task 3 - Bench-Scale Studies
- Task 4 - Economic Analysis

Foundational concepts and supportive data for work on this project were derived from prior in-house S-CUBED supported research into the feasibility of liquid-liquid solvent extraction of pesticides from water.

APPROACH

The central focus of the approach described herein rests on the selection of high volatility, low (water) solubility solvents as extraction media. Specific solvents targeted for investigation during the course of this study (listed in order of descending polarity) were:

1. Butylchloride,
2. Isopropyl ether,
3. Diethyl ether,
4. Hexane, and
5. Pentane.

During the course of this study, each of these candidate solvents were evaluated as extraction media for use in the bench-scale experiments.

In contrast to the above list, the solvent extraction media generally employed in commercial liquid-liquid extraction systems are much less volatile and usually considerably more soluble in the treated matrix. Examples of typical solvents used in industrial liquid-liquid extraction system include nitrobenzene, cresol, phenol, furfural, and blends of benzol-sulfur dioxide. In such systems extraction frequently takes place at elevated temperatures and steam stripping of the raffinate and/or extract may be required for solvent recovery or increased purification.

While the theoretical and technical aspects of this technology are highly refined on a commercial level, negligible consideration has been devoted to applications in pollution control technology areas. This is partially due

to the highly specialized nature of the solvents required and also to the costs and further environmental problems associated with steam stripping, and solvent reclamation. Also, very little attention has been given to the use of solvent extraction for removal of trace-level constituents in process effluent streams.

The SEXOP approach attempts to address these issues through use of solvent systems which can be employed at ambient temperature and which can be stripped and recovered easily due to low water solubility and high volatility.

Task 1 - Literature Review

A literature review was conducted at project initiation with approximately a two-month term allocated for the bulk of the search and a low level of effort allocated over the remainder of the project to keep the file current. The purpose of the literature review was to acquire information concerning:

- Those pesticides which are the most environmental significant, either because of their high toxicity ranking or because they are manufactured in large quantities.
- Candidate solvent systems which can be employed effectively in continuous liquid-liquid extraction systems.
- Continuous liquid-liquid extraction engineering process designs.
- Economic considerations with respect to solvent selection and process design.

At the initiation of the literature review a special category was set aside for each of the above four areas of study. This resulted in the formulation of an annotated bibliography

structured according to:

- Subject category,
- Reference in alphabetical order by author,
- Brief bibliographic statement.

This annotated bibliography, containing more than 60 references is included in the NTIS Report resulting from this research effort (1). Many of these citations contributed greatly to the work discussed herein and acknowledgment to this effect is documented in the above referenced report.

Task 2 - Screening Extraction Studies

Based on information derived from the Task 1 - Literature Review, the solvents and pesticides identified as experimental candidates were procured for screening extraction studies.

The screening extraction studies were conducted using a single batch storage extraction of water containing a known quantity of dissolved pollutant under investigation. The organic phase was then isolated and the quantity of pollutant extracted was determined using electron capture gas chromatography (EC/GC). The resulting EC/GC data was compared to the pollutant concentration in the aqueous phase and the partition coefficient (K_p) for each solvent system was then calculated. These calculated partition coefficient data were reviewed in order to select the most promising solvent/pesticide combination for use in the Task 3 - Bench-Scale Studies. Table 1 presents some criteria used for the selection of solvent for the bench-scale study.

Viewing Table 1, the kind of trade-offs required in the solvent selection process become readily apparent. While n-butylchloride is an excellent solvent from the standpoint of water solubility and K_p value, the boiling point is

high and the cost in terms of dollars per gallon is relatively high. Both of the ethers have attractive K_p values and costs but water solubilities are high and the ever present danger of peroxide formation and explosion constitutes a substantial safety consideration.

TABLE 1. CRITERIA USED FOR THE SELECTION OF SOLVENT FOR THE BENCH-SCALE STUDY

Solvent	Solubility in Water (\$)	Boiling Point (°C)	\$/Gal	K_p (Theoretical Value)			
n-Butylchloride	0.02	78.4	3.20	DDT ¹	370,000	Difuron	95.1
				Toxaphene	160,000	2,4-D	5.7
				Chlordane	240,000	Bromacil	28.7
				Herflurazone	200	Glyphosate	0.03
Isopropyl Ether	0.2	68	2.50	DDT ¹	230,000	Difuron	53.3
				Toxaphene	140,000	2,4-D	84
				Chlordane	84,000	Bromacil	10.7
				Herflurazone	61	Glyphosate	0.048
Hexane	0.03	69	2.40	DDT ¹	320,000	Difuron	3.5
				Toxaphene	74,000	2,4-D	0.02
				Chlordane	11,000	Bromacil	1.32
				Herflurazone	17	Glyphosate	0.111
Pentane	0.01	36	3.00	DDT ¹	270,000	Difuron	3.0
				Toxaphene	39,000	2,4-D	0.19
				Chlordane	26,000	Bromacil	1.29
				Herflurazone	27	Glyphosate	0
Diethyl Ether	6.9	34.5	2.70	DDT ¹	960,000	Difuron	182
				Toxaphene	180,000	2,4-D	65.9
				Chlordane	130,000	Bromacil	18.1
				Herflurazone	190	Glyphosate	0.109

¹DDT is no longer manufactured in the U.S.

After consideration of all of the solvents selected for study, it was decided that hexane probably represents the best overall compromise. Its water solubility and cost are both low, most K_p values are on the high end of the range, and the boiling point (while higher than would be desired for optimum conditions) is tolerable.

Referring again to Table 1, it will be noted that the eight pesticides selected for study cover a broad general range of K_p values. This diversity in K_p values was chosen intentionally in order to challenge the scope of applicability of SEXOP. While it is predictable that extraction efficiencies would be high for species with large K_p values, it is not clear at which point efficiencies become unacceptable for lower K_p values. It should be stressed, however, that K_p

value was not the only criterion for pesticide selection. The selection process also included ranking pesticides as a function of environmental significance either because of high toxicity rating or because they are manufactured in large quantities. It should be noted that for the purpose of brevity the term "pesticide" is used herein to denote both pesticide and herbicide species.

Task 3 - Fabrication of the Bench-Scale Device and Conduct of Experimental Process Runs

The liquid-liquid extraction process design configuration selected for the bench-scale system was of the "continuous differential contactor" variety. All differential contactor designs utilize a two-phase counter-current flow technique wherein the material of greater density is introduced at the top of an extractor unit and the material of lesser density is introduced at the base. Within this category, S-CUBED elected to design and fabricate a rotary disk contactor (RDC) having determined that this design configuration would optimize extraction efficiencies.

Figure 1 is an illustration of one RDC stage. A total of four stages comprise the column with the outer shell of the RDC unit consisting of a stainless steel (SS) pipe four feet in length and three inches in diameter. An explosion-proof motor is mounted about one foot above the top end plate of the RDC. Ball-bearings support the shaft just above a flexible coupling which connects the motor shaft to the RDC shaft. The motor is connected with a variable-speed controller in order to permit a variable range rotational speed with a maximum of 1,750 revolutions per minute (RPM). The stator-ring cluster, also shown through the view port in Figure 1, consists of a series of rings which are 0.035-inch thick with an outside diameter slight-

ly less than a three inch inside diameter of the RDC shell. The stator centerline holes are two inches in diameter. The stators are held in position by three 3/16-inch rods running the entire length of the column. One inch spacers are used to separate the stators, and threaded tightening nuts are used at each end of the rods. A mid column bearing is installed to minimize vibration of the rotating shaft. The bearing is held in position by three 3/16-inch rods and is constructed from a center-punched teflon disk. Peripheral to the RDC unit is a counter-current solvent stripper which, when fully assembled, is four feet in length and three inches in diameter. It is composed of assembly sections one foot in length to increase or reduce the total length, as needed, depending on efficiency conditions during experimental runs. The packed bed of the column consists of six-millimeter glass beads to simulate the packings used in commercial-scale strippers with the intent of providing a larger surface area with sufficient void space to permit efficient liquid and inert gas (nitrogen) counter-current flow.

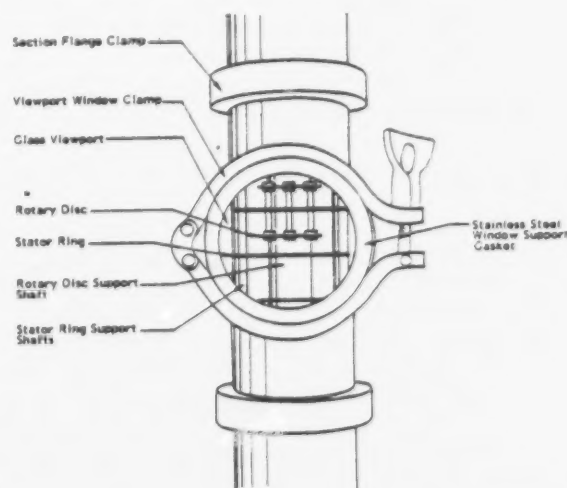
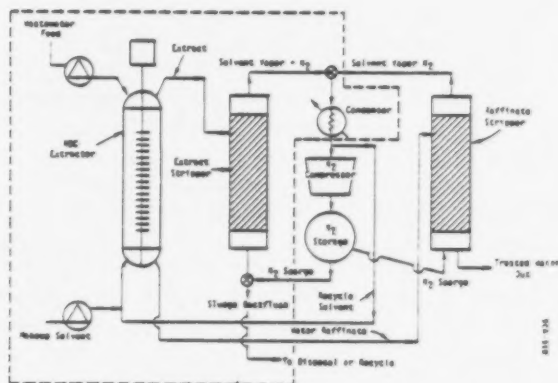


Figure 1. Close-up View of the Rotary Disc Contract.

Nitrogen and solvent vapor emitted from the top of the stripping column are introduced into a multiple-loop water cooled condenser which is made of 0.5-inch SS tubing. The condensed solvent is accumulated in a collection basin which is also fabricated from SS. Reclaimed solvent from the collector is recirculated to the RDC.

A flow diagram illustrating the configuration of the current bench-scale system is presented in Figure 2. Also shown in Figure 2 are the components, which would have to be added to the existing bench-scale configuration in the fabrication of a pilot or larger scale SEXOP system.



Note: Process components within the dashed line represent the configuration of the current bench-scale system. Components exterior to the dashed line represent projected requirements for a commercial scale system.

Figure 2. SEXOP Process Configuration.

SEXOP Runs Using Synthetic DDT Solutions

Following fabrication of the bench-scale SEXOP device, preliminary check-out runs were conducted to ensure operability of the integrated system as a whole. Once the process check-out phase was complete and operational integrity was assured, the next step in the research plan involved the conduct of SEXOP runs using synthetic saturated DDT solutions. These solutions were

formulated in ten gallon batches and were used to simulate extractor feed-stock until the full volume was depleted through the course of one or more runs. Individual runs were from two to three hours in duration and the exchange rate per hour (i.e., full RDC column volume exchange) ranged from about 1.4 to 3.5. The total RDC column volume is 1.27 gallons (4.8 liters). The list of experimental variables pertinent to each SEXOP run is as follows:

- Rotary disk shaft motor speed,
- Nitrogen stripper flow,
- Solvent to water ratio,
- Number of RDC column volume exchanges per hour.

These experimental variables were used to formulate standardized engineering run sheets which were subsequently used for all bench-scale experiments performed throughout the remaining duration of the project. A total of five synthetic DDT runs were conducted using the bench-scale system. In all cases extraction efficiencies in excess of 99.9 percent were realized using saturated DDT solutions as starting material. Data for a typical extraction run is presented in Table 2 and is accompanied by gas chromatographic data in Figure 3 to illustrate the extraction efficiencies graphically, for starting material and T₅ corresponding to Table 2.

In light of the excellent extraction efficiencies attained during the synthetic DDT runs using the hexane solvent, it was decided to proceed to the next phase of the activity involving test runs using real-world pesticide manufacturer effluent samples.

TABLE 2. EXTRACTION RUN NO. 4 USING SATURATED SYNTHETIC DDT SOLUTION AND A MOTOR SPEED SETTING OF 70

Sample I.D.	Retention Time	Contaminant Peak Areas	Raffinate ¹ Contaminant Concentration (%)	Extraction ² Efficiency (%)	
Starting Material	8.94	16,745,764			
	9.61	6,598,309			
	10.28	872,096			
	11.41	30,251,672			
		54,467,841	NA	NA	
Raffinate Sample No.	T ₀	9.09	42,426		
		9.76	17,891		
		11.59	152,333	0.391	99.61
			212,670		
	T ₁	9.17	29,351		
		9.84	21,472		
11.69		125,247	0.323	99.58	
		176,070			
T ₂	11.8	10,751	0.020	99.98	
T ₃	No Discernable DDT Peaks		—	99.99...	
T ₄	11.99	8,094	0.015	99.99	
T ₅	No Discernable DDT Peaks		—	99.99...	

NOTES:

$$\text{Raffinate}^1 \text{ Concentration (\%)} = \frac{T_0}{\text{Starting Material}} \times 100; \quad \% \text{ Extraction}^2 = 100 - \% \text{ Raffinate Concentration}$$

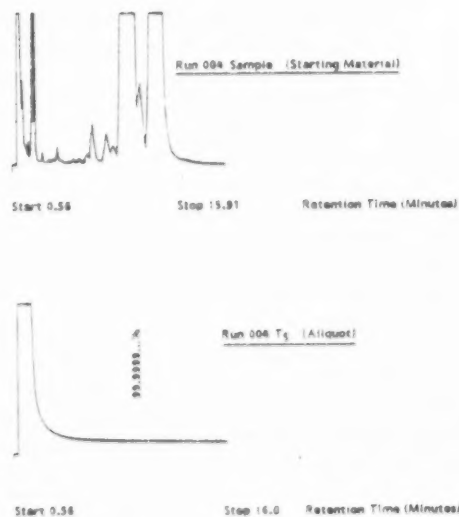


Figure 3. Gas chromatograms for starting material and T₅ corresponding to Table 2.

SEXOP Runs Using Real-World Pesticide Effluent Samples

At the initiation of the bench-scale fabrication activity, a parallel effort was underway to acquire pesti-

cide effluent samples from various U.S. manufacturers. With the assistance of the Environmental Protection Agency (EPA) three 55-gallon samples were acquired from the respective manufacturers of: DDT, 2,4-D, and bromacil. The DDT effluent sample was used for all experimental runs addressed by this paper; the 2,4-D and bromacil samples were held for study on future research projects. The DDT sample used for experiments in this study consisted of raw alkaline wastewater generated from (1) the neutralization and water washing of molten DDT, (2) pump drips and leaks, (3) spent caustic solutions from fume scrubbers, and (4) small quantities of miscellaneous non-sewerable wastes collected throughout the plant. The plant was operating normally at the time of sample acquisition and sampling was done at the end of the process at the waste collection tank prior to any control technology.

Gas chromatography/mass spectroscopy (GC/MS) analysis of the DDT process water sample was conducted using a Finnigan 4021 GC/MS with an INCOS data system. Three percent OVI column on 60/80 chromosorb was used as column material. The temperature program was set from 50°C to 275°C at a rate of 8°C per minute. Analysis results indicated that chlorinated hydrocarbons (chlorinated benzenes, phenols) were the dominant species in the DDT process water. A total of 52 discrete compounds were identified including many isomers of DDT, DDD and DDE compounds (17.26 percent) with the amount of chlorinated benzene compounds totaling 69.4 percent of the total extractable organic constituents.

The bench-scale run extraction procedure involved thorough mixing of the barrel sample for a 24-hour period prior to the run with continued mixing while the run was in progress. The mixed sample contained approximately 20 to 25 percent suspended solids, had a pH of 11, and was somewhat viscous

due to a high content of solubilized organic and halo-organic compounds.

A total of four runs were conducted using this sample with progressively higher extraction efficiencies for each run resulting from optimization of operational variables and engineering design. Table 3 presents a summary of representative bench-scale runs from this sequence. Figure 4 presents gas chromatograms from Bench-Scale Run No. 9 showing the starting material and Aliquot No. 5, respectively.

TABLE 3. BENCH-SCALE EXTRACTION RESULTS FOR RUNS 006, 009, AND 010

Run Number	Extraction Results
006	First bench-scale run on a process effluent sample. Results were only moderately successful in that many constituents were not significantly reduced.
009	Very positive results. All peaks with exception of the 6.02 minute retention time constituent were in the mid-to-upper 90th percentile extraction efficiency range. The peak with the 6.02 minute retention time was extracted at an efficiency of about 80 percent.
010	Most successful of all runs in that the majority of constituents were removed at efficiency levels exceeding 99 percent and there were no removal efficiencies below 90 percent.

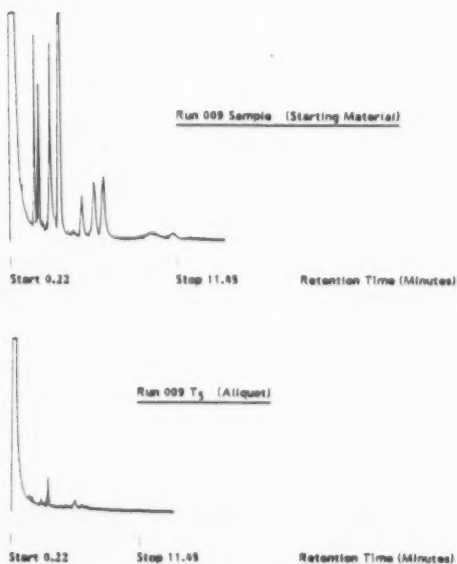


Figure 4. Gas chromatograms from bench-scale Run No. 9 showing the starting material and Aliquot No. 5.

RESULTS AND CONCLUSIONS

The purpose of this study was to test the hypothesis that solvent extraction, using high volatility solvents for the removal of pesticides and other organic constituents from process streams, would be commercially feasible both technically and economically. Subsequent to fabrication of the bench-scale system, a series of ten studies were conducted using both synthetic and real-world process effluent DDT samples. Studies using the synthetic samples resulted in a clean up (i.e., extraction efficiency) in excess of 99.9999 percent. Subsequent to process optimization, bench-scale runs using a real-world process effluent DDT sample resulted in a clean-up for most constituents in excess of 99 percent. No constituents in the sample (of the best-case final run) were extracted at an efficiency below 90 percent. Data in support of these findings are presented in an NTIS report (1). It should be stressed that the process effluent samples consisted of raw untreated wastewater which GC/MS analysis revealed to contain at least 52 components. Based on the high extraction efficiencies resulting from the bench-scale runs using DDT and the generally favorable extraction coefficients for the pesticides examined during the screening extraction studies, it can be concluded that SEXOP technology is potentially applicable to other constituents with similar K_p values. An examination of the detailed chemical composition of available in-house effluent samples shows that many of the same constituents present in the DDT sample are common to other wastes as well. This would indicate a broad-range applicability of SEXOP to a variety of highly contaminated samples. At the time of this writing continuing research is underway to define more clearly, the boundaries of applicability for this process.

In light of the technical results of SEXOP with the synthetic and process effluent DDT samples, an economic analysis of the process was undertaken to develop an economic basis for the technology. This was accomplished using a two-fold approach: (1) based on current knowledge, an engineering cost estimate was projected for both a large and a small commercial-scale SEXOP process; and (2) these cost projections were compared with the more firmly established capital and operational costs associated with carbon adsorption technology. This study revealed that the cost of SEXOP technology compares favorably with the carbon adsorption alternative.

A projected large SEXOP plant should be able to process 301 million gallons/year at a cost of \$2.02/1,000 gallons. Information derived as a result of the literature review effort has shown that, based on total annual cost, carbon adsorption may require from \$1.15 to \$230.00 per thousand gallons of effluent processed. The most common value cited is around \$7.00/1,000 gallons. Based on the overall number of citations, in the literature studied, the most realistic range lies between \$3.00 to \$10.00 per thousand gallons of effluent treated. There are a number of reasons for the discrepancies in the literature for capital equipment and O&M costs for carbon adsorption. Some process variables which play an important role in the wide range of carbon adsorption effluent treatment costs include:

- Concentration of pollutant in the stream being treated.
- Size of the facility (\$/1,000 gallons treated tend to decrease as the size of the facility increases).
- Whether the carbon is disposed of or regenerated and if regenerated, whether this is done on site or at a central location.

- Location of the facility.
- Effluent purity objective.

Bearing these discrepancy factors in mind, however, and using the lowest number for carbon adsorption, current projections indicate that SEXOP still maintains an attractive economic position.

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BIOLOGICAL REMOVAL OF MERCURY FROM TOXIC WASTE

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ABSTRACT

Mercury resistant bacteria have been applied to the biological treatment of mercury-contaminated waste. The approach was to use mercury resistant bacteria to reduce Hg^{2+} to Hg^0 . After preliminary batch culture studies, a pure strain of mercury resistant *Escherichia coli* was introduced into a bioreactor equipped with a pump for adding $HgCl_2$ in-line. Using nonsterile, urban sewage (average BOD_5 135 mg/l) in a continuous operation, it was found that the bacteria could remove mercuric ion for periods of over 2 weeks at the rate of 2.5 mg/l-h. If the effluent was allowed to set at room temperature for an additional 24 h after exiting the bioreactor, 98% of the added mercury (70 mg/l) was removed. Examination of the microbial population 24 h after the initiation of the process indicated that the original strain of *E. coli* had been replaced by other species of bacteria. A random selection of the predominant organisms were analyzed for antibiotic and mercury resistance. There appeared to be some organisms which were Hg-resistant but did not volatilize mercury. The biological process was applied to an actual industrial sample from the chlor-alkali industry. Making only slight modification to our biological process, we were able to completely detoxify this material using the mercury resistant bacteria. These results indicate the feasibility of the biological approach to the control of industrial mercury pollution.

INTRODUCTION

Toxic and potentially hazardous heavy metals are found in wastewater from many industrial sources. Among these compounds, mercury is one of the most toxic and best understood examples of heavy metal pollution. From years of study, it is now apparent that the toxicity of mercury is dependent upon the chemical form in which it occurs. In general, the organic mercury compounds are much more toxic than the inorganics. Of the organomercurials, methylmercury is perhaps the most problematic since it is naturally formed in the aquatic and terrestrial environments from elemental and mercuric mercury. Most important from the standpoint of this

report, it has been shown that the environmental local load of methylmercury may be considerably increased by industrial release of inorganic mercury (1). Thus, mercury represents an example of a pollutant which is converted into a more toxic substance when released into the environment. Hence, we believe that serious consideration should be given to the concept of complete removal and recovery for reuse, rather than "secure" burial, when dealing with compounds such as mercury.

Mercury is currently removed from industrial wastewater by chemical precipitation (2-6). A widely used

method involves the addition of sodium sulfide into mercury laden water. The insoluble mercuric sulfide which forms is then removed as a sludge. Another method which has been employed uses sodium borohydride to reduce the mercury to its metallic form which is then filtered from the effluent.

Microbiological methods for the extraction and recovery of metals have previously been proposed (7-9). Reported methods most often involve uptake or binding to the micro-organisms. Unfortunately, these approaches suffer from the same disposal problem mentioned above. Alternatively, we propose the use of mercury resistant bacteria which are capable of converting Hg^{2+} to the volatile elemental form (10-12). The volatile, metallic mercury thus produced could then be vented for recovery. Since the bacteria used for the reduction of mercury are aerobic, the removal of volatile mercury is facilitated by the aeration required to maintain bacterial growth.

APPROACH

Bacterial Strain and Growth Medium

The mercury resistant organism used in these experiments was Escherichia coli KP245 which harbors the mercury resistance plasmid pRR130. Although every experiment was initiated with this organism, prolonged growth under the nonsterile conditions used in our experiments normally resulted in the development of a mercury resistant mixed-culture.

The bacteria were grown and maintained on media containing yeast extract (0.5 g/l), sucrose (6 g/l) and $HgCl_2$ (5 mg/l). The sewage used was collected from a residential subdivision of about 300 homes with no industry or other commercial

enterprise and was screened before use.

Experimental Apparatus

The bioreactor was a New Brunswick Scientific Microferm MF 115, 14l fermentor equipped with variable mixing and aeration, as well as automatic temperature and liquid level control. The two paddle mixer was operated at ca. 120 rpm, while the liquid temperature was maintained at 37°C. The aeration rate was 2 l/min into a 5l working volume which kept dissolved oxygen at over 8 ppm for all cultivations reported. The pH remained within an acceptable range without adjustment.

Mercury Analysis

Mercuric ion concentrations were routinely monitored spectrophotometrically by the dithizone assay as described previously (13). The assay was determined to be sensitive enough for the higher concentrations of mercury used in this study. Some samples were submitted for wet ashing (1:1 mixture of $HNO_3/HClO_4$) and analysis by inductively coupled plasma (ICP) emission spectrometry at the Ohio Agricultural Research and Development Center (Wooster, Ohio).

RESULTS

Our initial studies examined the growth and mercury removal characteristics of shake-flask cultures of a strain of E. coli (KP245) selected for its high tolerance to mercuric ion. It was shown (Fig. 1) that increasing the concentrations of mercuric ion up to 10 mg/l increased the lag phase, but had no apparent effect on the growth rate. In other studies, the rate at which the mercuric ion was removed from the culture flasks was also examined. In these experiments, an overnight culture (grown on 10 mg/l

Hg^{2+}) was harvested, washed twice, and resuspended in fresh growth medium in the presence of 10 mg/l Hg^{2+} . Samples were removed at various times and assayed for Hg^{2+} . The results from these experiments (Fig. 2) demonstrated that immediately following inoculation the mercuric ion concentration decreased very rapidly, during which time there was no observed growth. However, after most of the mercury was removed (within 1.5 hours), normal growth resumed.

In order for this process to be applicable to industrial situations, it was necessary to determine whether continuous mercury removal under non-sterile conditions was feasible. These studies were performed with the bench scale bioreactor described above. Each experiment was initiated by adding 5l of raw sewage, (average $\text{BOD}_5 = 135 \text{ mg/l}$) to the bioreactor along with 100 ml of the starter culture. Refrigerated sewage was then pumped into the bioreactor on a continuous basis at the rate of 5l/24 hours and a concentrated solution of HgCl_2 was mixed in-line with the sewage at an adjustable rate which allowed us to control the concentration of Hg^{2+} in the influent. Under these conditions, we found that 70 mg/l Hg^{2+} in the influent was a safe, upper limit for extended cultivations although the bacteria were able to reduce as much as 100 mg/l over 12-14 h time periods. However, if Hg^{2+} was maintained continuously at this level the biological reduction process would eventually slow or collapse entirely.

Table I shows the results of one of three replications of two week, continuous cultivations using sewage as the growth medium and maintaining Hg^{2+} at 70 mg/l in the influent. Results for Hg^{2+} removal from the other replications were similar. Samples were removed daily and

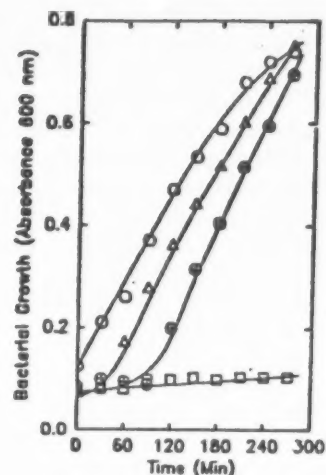


Figure 1. Bacterial growth at different concentrations of Hg^{2+} . After a 2% overnight inoculum, growth curves were determined at Hg^{2+} concentrations of: (o) 0 mg/l, (Δ) 2 mg/l, ($\square$) 4 mg/l, and ($\diamond$) 10 mg/l. With permission from Ref. 14.

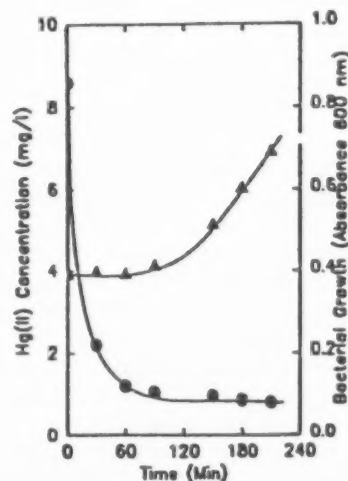


Figure 2. Reduction of mercury concentration and bacterial growth. ($\bullet$) Hg^{2+} concentration, ($\blacktriangle$) bacterial growth. With permission from Ref. 14.

analyzed for mercury content. The data indicated that the total mercury

concentration decreased to a low level in unsettled effluent held for an additional 24 hours after leaving the bioreactor (Table I). It can also be seen that during this entire period the average free Hg^{2+} concentration in the effluent was below the sensitivity of the dithizone assay ($< 1.5 \text{ mg/l}$). The ashing and inductively coupled plasma (ICP) analysis indicated a low concentration (1.2 mg/l) of total mercury in the effluent.

From these results, it was calculated that the bioreactor could remove Hg^{2+} from the influent sewage at the rate of 2.5 mg/l-h with an efficiency of 88%. By allowing the effluent to set at room temperature for an additional 24 hours after exiting the bioreactor (there was no significant settling during this time) we could remove 98% of the added mercury.

As another aspect of this study, we examined the bacterial population of the bioreactor 24 h after inoculation. The original E. coli strain was not detected at this time. If the mercury removal process was initiated in the absence of the starter culture of E. coli, there was no significant removal of mercury (data not shown). These results indicated that under nonsterile conditions the continuous removal of mercury was accomplished by a mixed-population of mercury resistant bacteria. Since the starter culture was required to initiate the process, the mixed population arose naturally at the reduced mercury levels maintained in the bioreactor, or else, genetic transfer from the starter culture must have occurred.

In order to better characterize the mercury-reducing, mixed-culture, we isolated 13 colonies at random from a 10^1 dilution on agar plates containing 10 M HgCl_2 . The isolated strains and their antibiotic

phenotype are given in Table II. Note that none of the strains share a similar antibiotic resistance profile with the original E. coli KP245 strain. This provides indirect evidence that intact plasmid transfer from E. coli is not important. The isolates were all resistant to mercury (Table III). However, the level of resistance varied considerably. Mercury resistance was also measured as a function of the chemical oxygen demand (COD) of the media. For this study, the COD was due to varying concentrations of glucose in the medium and, thus, it was used to reflect the amount of oxidizable material. As shown in Table III, most of the isolated strains had decreased mercury resistance levels at decreased COD values. However, for strains 9, 10 and 11, there was no association between COD and mercury resistance. Since mercuric reduction is an energy requiring process, decreased levels of resistance would be expected in media of low COD. Therefore, strains 9, 10 and 11 are mercury resistant, but probably do not reduce Hg^{2+} . Mercuric reductase was not detectable in these strains. Therefore, it appears that in the bioreactor there exists within the mixed-culture a mercury-resistant, nonreducing subpopulation. Further studies are required to determine the effect of this subpopulation upon mercury volatilization, especially at lower influent mercury concentrations.

More recently, we have applied our biological process to an actual industrial waste sample from a chlor-alkali plant in Northern Ohio. This sample of a filtrate "mud" from the electrolysis cells was mainly composed of potassium salts, insoluble metal hydroxide and 100-150 ppm of mercury in the form of mercury hydroxide. Mercury was successfully removed from this sludge using our process in both batch and continuous modes.

TABLE I. CONTINUOUS BIOLOGICAL REMOVAL OF MERCURY FROM SEWAGE OVER A TWO-WEEK PERIOD

Influent Hg^{2+} Concentration ^a	Average bioreactor Hg^{2+} Concentration (24 h detention time)		Average effluent Hg^{2+} Concentration (additional 24 h detention time)	
	Free Hg^{2+} ^b	Total Hg^c	Free Hg^{2+}	Total Hg
70 ±	< 1.5	9.6 ± 2.7	< 1.5	1.2 ± 1.0

^aAll Hg concentrations are in mg/l.

^bFree Hg^{2+} concentration was determined by the dithizone assay.

^cTotal Hg concentration was determined by wet ashing and ICP analysis.

In the batch process, a measured quantity of mud was diluted in water and the pH adjusted to 7 by adding concentrated sulfuric acid. This solution was then added to the bioreactor containing a mixed-culture of mercury resistant bacteria in nutrient broth. After addition of the diluted sample, the initial mercury concentration in the bioreactor was 3.5 mg/l. As shown in Table IV, the mercury concentration in the bioreactor decreased 89% over a 12 h period.

In the continuous process, the diluted waste sample and the nutrient broth solution were continuously pumped through two separate influent

lines to the bioreactor. The reservoir of diluted mud (6.5 mg/l Hg^{2+}) was mixed continuously to keep undissolved solids in suspension. The influent flow rate of the diluted mud into the bioreactor was 0.18 l/h. The nutrient broth was added from a separate line at the rate of 0.34 l/h. In 3 separate experiments, the bioreactor was allowed to reach steady-state after which data were collected over a 24 h period. In each of these experiments, the mercury concentration in the bioreactor was maintained at 0.25 mg/l, indicating that mercury was continually removed at an average of 0.22 mg/l-h.

TABLE II. ANTIBIOTIC RESISTANCE PROFILES OF RANDOM ISOLATES FROM THE BIOREACTOR

Strain	AM ^a	AN	B	C	E	K	NA	S	T
1. <u>Pseudomonas diminuta</u>	R ^b	S	S	S	R	R	R	R	S
2. <u>Staphylococcus haemolyticus</u>	R	S	S	S	S	R	S	R	S
3. <u>Pseudomonas diminuta</u>	S	R	R	S	R	R	S	R	S
4. <u>Staphylococcus epidermidis</u>	S	S	S	S	S	S	S	S	R
5. <u>Acinetobacter calcoaceticus</u>	S	S	R	S	R	S	S	S	S
6. <u>Acinetobacter calcoaceticus</u>	S	S	S	R	R	S	S	S	S
7. <u>Aeromonas hydrophila</u>	R	S	R	S	S	S	S	S	S
8. <u>Pseudomonas alcaligenes</u>	R	S	R	S	R	S	R	S	S
9. <u>Micrococcus luteus</u>	S	S	S	S	S	S	S	S	S
10. <u>Staphylococcus hominis</u>	S	S	S	S	S	S	S	S	S
11. <u>Staphylococcus haemolyticus</u>	S	S	S	S	S	R	S	R	S
12. <u>Alcaligenes odorans</u>	S	S	R	S	R	S	S	R	S
13. <u>Staphylococcus epidermidis</u>	S	S	S	S	S	S	S	S	S
14. <u>Escherichia coli, KP245</u> ^c	R	S	S	S	S	S	S	S	S

^aAntibiotics used were: ampicillin (AM), amikacin (AN), bacitracin (B), chloramphenicol (C), erythromycin (E), kanamycin (K), nalidixic acid (NA), streptomycin (S), and tetracycline (T).

^bR, resistant; S, sensitive.

^cUsed for the initial inoculation, but not recovered from the bioreactor.

TABLE III. MINIMAL INHIBITORY CONCENTRATION (MIC) OF MERCURY AS A FUNCTION OF COD^a

Strain	MIC (mg/l Hg ²⁺) Values					
	COD 19 600	COD 9 800	COD 4 900	COD 1 200	COD 300	COD 150
1	16	-	-	-	-	-
2	4	-	-	-	-	-
3	12	-	-	-	-	-
4	8	-	-	-	-	-
5	40	30	4	4	4	4
6	40	30	20	4	2	2
7	40	30	8	4	4	2
8	40	30	20	16	16	16
9	80+	70	70	70	70	70
10	80+	70	70	70	70	70
11	80+	70	70	70	70	70
12	40	-	-	-	-	-
13	40	-	-	-	-	-
14	40	30	20	4	4	4

^aCOD as mg/ O₂.

^b-, No growth detected.

TABLE IV
MERCURY REMOVAL IN A BATCH PROCESS

Time (h)	Influent Mercury (mg/l)	Mercury Removal (%)
0	3.5	0
3	2.0	42
6	1.5	56
9	0.9	75
12	0.4	89

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COMBINED POWDERED CARBON/BIOLOGICAL ("PACT") TREATMENT TO DESTROY
ORGANICS IN INDUSTRIAL WASTEWATER

(Case History of Du Pont Chambers Works 40 MGD Wastewater Treatment Plant)

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ABSTRACT

This paper discusses the 40 million gallon per day industrial wastewater treatment plant (WWTP) at Du Pont's Chambers Works site at Deepwater, NJ. This very large WWTP uses a Du Pont developed advanced technology to treat highly colored, acidic wastewater containing a wide variety of organic compounds, including priority pollutants. Many of these compounds are not susceptible to conventional biological treatment. The advanced technology is the patented Powdered Activated Carbon Treatment (PACT)⁽¹⁾ process, which is a combined secondary/tertiary treatment. It is accomplished by adding powdered activated carbon directly to an aerator, and then operating a combined biological oxidation/activated carbon adsorption process.

Some noteworthy features of the Chambers Works WWTP are reviewed, including a unique, 40 tons/day regeneration furnace for powdered activated carbon, and a "state of the art" double-lined secure landfill where primary sludge from the WWTP is deposited. Some performance advantages of the "PACT" process over conventional activated sludge treatment will be shown. Data on removal of priority pollutants is included. Some of the reasons that have led to the development of a rapidly expanding Du Pont Environmental Services business based on available capacity at the WWTP will also be discussed.

INTRODUCTION AND PURPOSE

This is a case study of a very large, successful industrial wastewater treatment plant which had to use innovative technology to meet required effluent quality at a reasonable cost. The "PACT" process,

which was developed for this purpose, did provide combined secondary/-tertiary treatment in a facility comparable to a conventional activated sludge plant in terms of investment and operating cost. The successful

(1)"PACT" technology is now owned by Zimpro, Inc., who are making it available under license. "PACT System" is a registered trademark of Zimpro, Inc.

treatment of Chambers Works highly colored, variable waste containing significant amounts of normally difficult to biodegrade organics by this technology may indicate advantages from its use in other treatment situations.

It is also a purpose of the paper to point out some unique advantages of a large, central, advanced wastewater treatment facility in treating a variety of outside wastes which may be unsuitable for smaller, local, less sophisticated treatment plants.

DISCUSSION AND RESULTS

1) Treatment Process

The waste stream which the WWTP was designed to treat in 1975 had the following average characteristics:

Flow	- 26,400 gpm
Soluble BOD ₅	- 88,700 lbs/day (280 mg/l)
Color	- 1,000 APHA
Acidity	- 227 tons/day* (1,430 mg/l)
Dissolved Organic Carbon	- 65,000 lbs/day (205 mg/l)
Total Dissolved Solids	- 2,000 to 3,000 mg/l
Total Suspended Solids	- 40 tons/day** (258 mg/l)

*Acidity concentrations or weights are expressed as CaCO₃ equivalents throughout this paper.

**Included 28 tons/day by-product solids from lime neutralization.

This waste stream represented the combined discharge from Chambers Works plus the adjacent Carney's Point site, which has since closed. While this was only a medium strength waste in terms of BOD concentration, the organic component of the waste stream was particularly difficult to treat. It contained a variety of aromatic compounds, and the composition of the organics was continually changing because of the batch nature of many of the Chambers Works operations, particularly in the dyes area.

Du Pont constructed a \$45 MM WWTP to treat this waste. Current replacement value is over \$100 MM. Figure 1 is a diagram of the facility. The WWTP operates 24 hrs/day and 7 days/week. It is staffed with 26 chemical process operators and an approximately equal number of clerical, maintenance, electrical, and instrument personnel. There are approximately 15 supervisory and technical people assigned to the WWTP.

a) Primary Treatment

A three stage treatment process was specified. In primary treatment the acidic water is neutralized with lime in a single stage neutralization using three, stirred 200,000 gallon reactors operated in parallel. The WWTP receives powdered lime by rail car or truck. Powdered lime is stored in 4 large silos and is slaked to 8-10% concentration as needed. Lime slurry is fed to the neutralizers by an automatic control system that maintains pH at any preset level. The WWTP currently consumes approximately 60 tons/day of dry lime to treat 100 tons/day acid. The plant has enough capacity to treat over 200 tons/day acid.

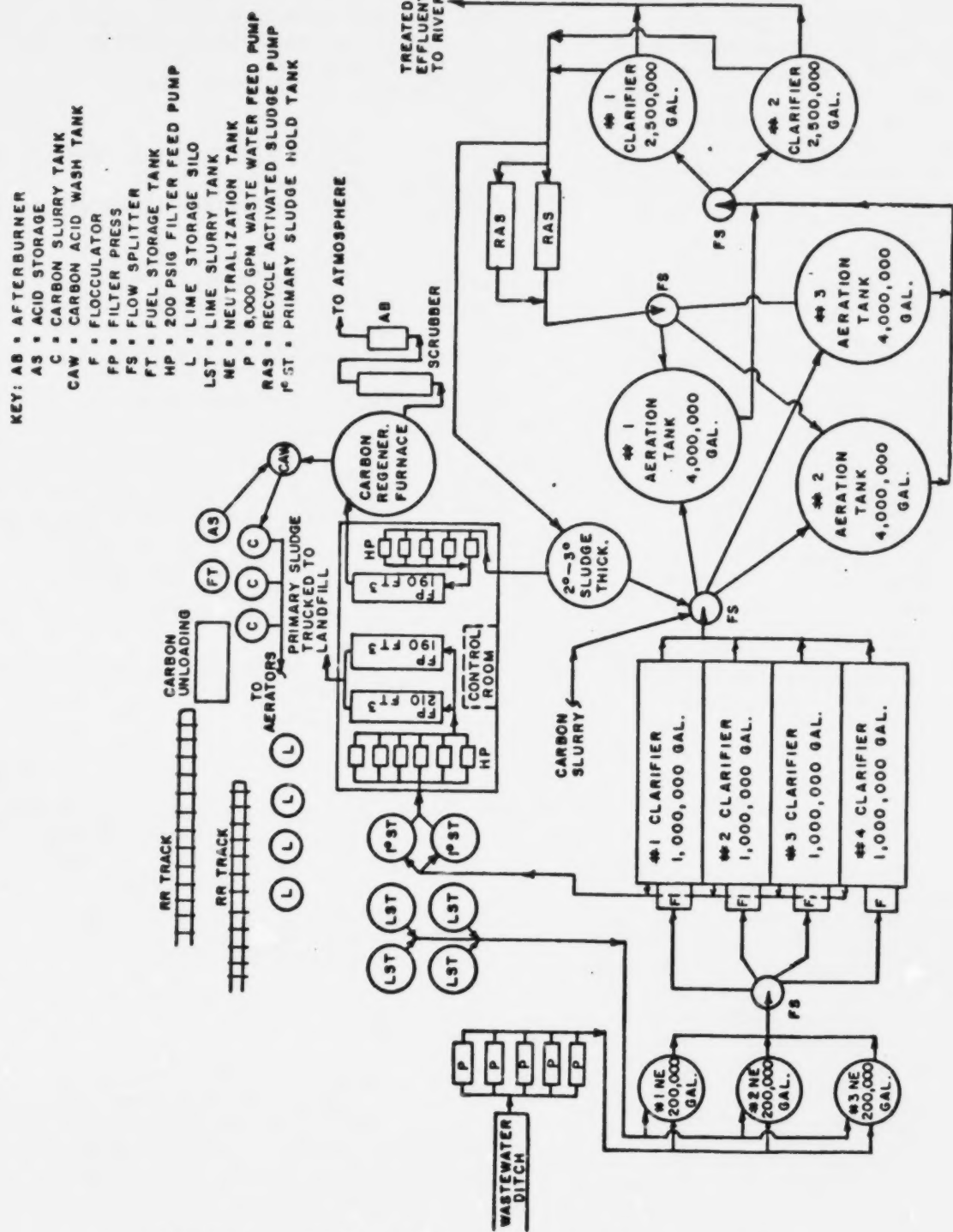


Figure 1. Chambers Works Wastewater Treatment System

The neutralizers overflow to four primary clarifiers, each one million gallons in size. The rectangular clarifiers operate in parallel and are 230 by 55 by 12 feet deep. Solids in the wastewater feed, as well as by-product solids formed during neutralization, settle and are removed as an 6-10% slurry in the clarifier underflow. After filtration to a 45 to 50% solids cake, the solids are hauled to the Secure Landfill. Two high-pressure, (210 psig at end of cycle) large recessed chamber filter presses make approximately 7 tons of wet press cake per 30 to 60 minute cycle.

The WWTP currently generates from 50 to 70 tons/day (dry basis) solids, equivalent to 50,000 yd³/year of landfill volume. The solids are mainly inorganic, primarily calcium and magnesium salts, as well as silica compounds from river water silt. These solids also contain small amounts of heavy metals and a variety of organic compounds. The solids are an inevitable by-product of the primary treatment process, and because they are primarily inorganic compounds, the only feasible disposal method is landfilling.

b) Secure Landfill

Figure 2 is a diagram of the landfill. A double liner of a chlorosulfonated polyethylene material, "Hypalon", covers the entire bottom and part of the sides of the landfill. Collection pipes between the liners serve as leak detectors and drain to sumps outside the landfill. The sumps are sampled on a regular basis for any signs of contamination. Above the top liner is a similar collection system for leachate which is pumped back to the WWTP. The landfill will ultimately become a 70 feet high pyramid with a 15 acre base.

As outer sections of the landfill are filled, the edges and top are covered with a 2 feet layer of essentially impervious, permeability of less than 1×10^{-7} cm/sec, clay and 12 inches of top soil.

A controlling factor in the operation of the primary filter presses is that the filter cake must meet rigid soil stability criteria. These solids have to support the weight of heavy earth-moving equipment. Further, the allowable slope of the landfill sides, and hence the volumetric capacity of the landfill, is closely regulated to assure a large safety factor against any possible slippage along the slopes.

As backup protection, there are 26 monitor wells located around the landfill; and in the very unlikely event of a double liner failure, interceptor wells would be utilized to prevent any harm to the environment while the problem was corrected.

c) "PACT" Secondary/Tertiary Treatment & Carbon Regeneration

The neutralized wastewater that overflows the primary clarifiers flows into three, four million gallon aerators operated in parallel. These are 185 feet diameter, 20 feet deep vessels. Here over 90% of the BOD is removed by a slurry of suspended solids; the solids consisting of an approximate 50/50 mix of bio-mass and activated carbon. Approximately two million pounds of solids are under aeration. Air for the biological oxidation is supplied from large blowers that normally maintain a dissolved oxygen concentration of 1 to 7 ppm in the water by forcing 5,000 to 15,000 standard cubic feet per minute air through

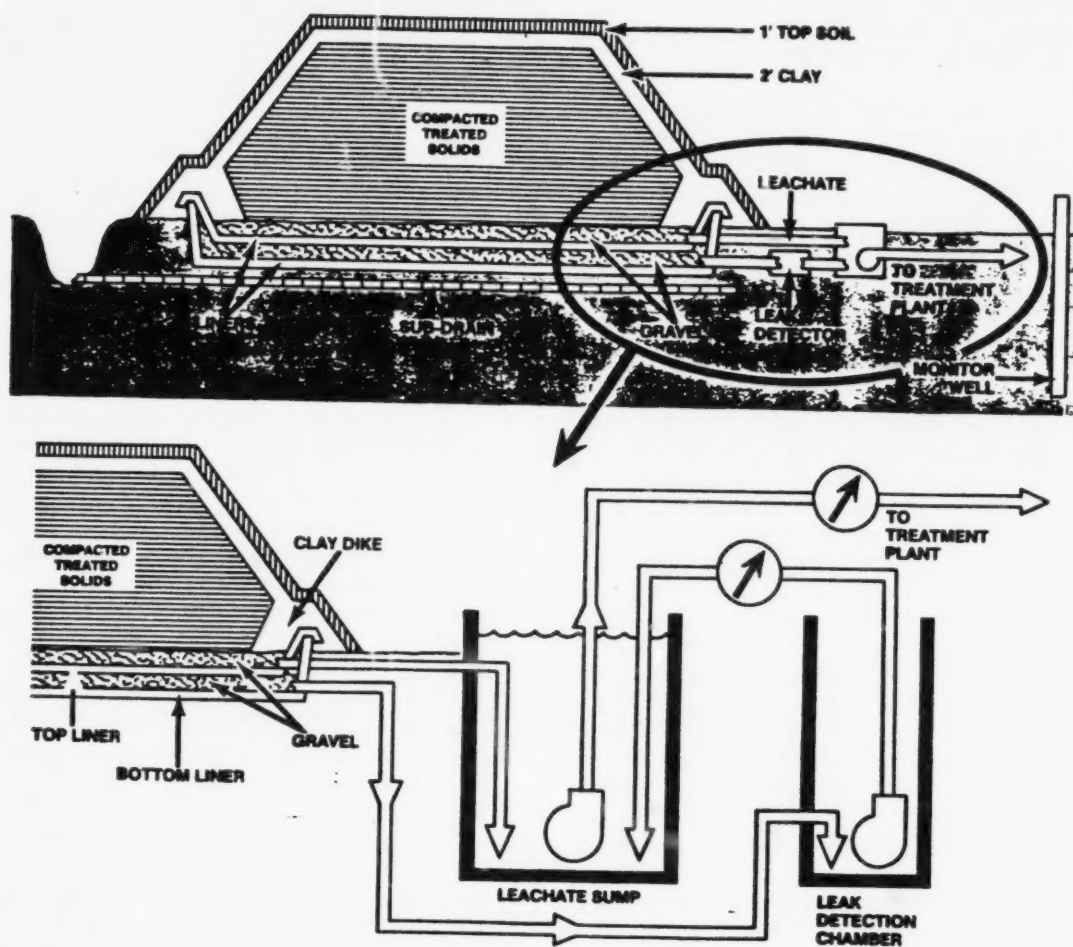


Figure 2. Secure Landfill

diffuser pipes in the bottom of each aerator. The electric bill to run the blowers for just one aerator is over \$150M/year. The water is decolorized, and because of the presence of the carbon, organic compounds that normally are not susceptible to biological oxidation by bacteria are removed.

The aerators overflow to two 2.5 MM gallon parallel clarifiers. These are circular, 172 feet diameter by 15 feet deep tanks. The bio-mass/carbon solids settle and are pumped back to the aerators. This recycle of bio-mass is the key to the activated sludge process, as it allows the WWTP to maintain an average of five to forty days of residence time for solids in the aerators. This gives the bacteria time to acclimate to the organics in the wastewater and then consume them. By comparison, the hydraulic residence time of the wastewater in the aerators is in the range of five to nine hours.

Up to 3 million pounds per year of virgin activated carbon are needed for the "PACT" process at Chambers Works. It is delivered as a dry powder by rail car and stored as a one lb/gallon aqueous slurry before use. The carbon is added to the wastewater just before it enters the aerators.

As the bacteria consume over 40,000 pounds/day of dissolved organics they multiply and generate approximately 6,000 pounds/day of new bio-mass. Combined with the continuous feed of powdered carbon, this imposes a net solids increase of over 12,000 pounds/day into the aerators. There must be an equivalent purge of solids from the system, and this is provided by removing a side stream from the concentrated solids underflow from the secondary clarifiers.

The WWTP has the capability of regenerating powdered activated carbon from these wasted secondary solids. This is another unique feature of the WWTP, as the powdered activated carbon is regenerated in a multiple hearth furnace. To our knowledge this is the only commercial use of a multiple hearth furnace to regenerate powdered carbon.

When regenerating carbon, wasted "PACT" sludge is filtered prior to being fed to the furnace. The same type filter press is used for "PACT" sludge as is used for primary sludge. The design solids concentration of the bio-mass/carbon filter cake was 35%, but in actual practice higher solids concentration, 45%, was achieved with the "PACT" sludge. Without the presence of carbon as an internal filter aid, it would be difficult to get over 25% solids concentration.

After filtration to a 45% solids cake, the bio-mass/carbon solids are conveyed to the top of a 40 feet high by 26 feet diameter, five hearth furnace. Under controlled conditions, the solids are fed down through the furnace, being raked across each hearth by rabble arms mounted on a large, rotating center shaft. Water is first evaporated and then bio-mass and adsorbed organics are burned. Finally at the bottom of the furnace at approximately 1,000°C, and in the presence of steam, the powdered carbon is regenerated. The incandescent carbon is quenched in water, washed with acid to remove inorganics, and recycled to the aerators. Heat to the furnace is supplied from an external, oil fired burner. The heated gases rise through the furnace countercurrent to the solids. Gas flow must be controlled to avoid blowing powdered carbon out of the top of the furnace.

To control air pollution, the furnace off gas is scrubbed with water and then passed through an afterburner at about 700°C.

During the initial years of operation there were significant processing problems with the furnace itself, as well as with the "PACT" sludge filtration and conveying systems. Once modifications to equipment and process control instrumentation were completed, the furnace generated 13 T/D of activated carbon with an average iodine number of 400* over a two year period of operation. This represented a quality yield of about 80%. During this period the furnace was fed 50 T/D of wet sludge cake, and destroyed over 10 T/D bio-mass, adsorbed organics, and unrecovered carbon.

The furnace is currently out-of-service. A combination of reduced organic loads from the Chambers Works (hence, lower carbon dosages are needed to assure adequate organic removal) plus currently very favorable prices for virgin activated carbon make it more economical to use only virgin carbon on a once through basis. Currently, wasted secondary carbon/bio-mass sludge is recycled to the inlet wastewater feed stream. The wasted secondary solids then become part of the primary sludge, are removed in the primary clarification step, and are ultimately deposited in the Secure Landfill.

*An industry measure of adsorptive capacity for certain types of molecules. The higher the number the greater the adsorptive capacity.

2) Performance of the "PACT" System

The "PACT" process was developed in 1970 from technical studies to develop a treatment process for Chambers Works wastewater. As compared with a conventional activated sludge process for treating Chambers Works wastewater, the "PACT" process:

- Gave consistent BOD removals of over 94%
- Raised DOC removal from 62% to 85%
- Reduced color
- Reduced foaming in the aerators
- Improved the settling and filtration properties of the secondary solids
- Protected the bacteria from shock loads of organic compounds

Typical comparative data from continuous laboratory test units are shown in Table I. As would be expected, performance improved with increasing carbon dose up to a certain level.

The combined second/tertiary treatment with "PACT" resulted in large investment and operating cost savings as compared with a conventional tertiary treatment process using biological oxidation followed or preceded by adsorption in granular carbon columns. In effect, the "PACT" process gave tertiary treatment quality effluent in a single carbon adsorption/bio-oxidation aeration process.

TABLE I

TABLE I. LABORATORY DATA COMPARING "PACT" VS. ACTIVATED SLUDGE

	Feed	Effluent		
		"PACT" Activated Sludge	"PACT" 25 PPM Carbon Dose	"PACT" 100 PPM Carbon Dose
Soluble BOD ₅ , mg/l	111	7.5	6.6	6.1
BOD Removal	-	93.2%	94.1%	94.5%
DOC, mg/l	86	31.9	21.7	13.1
DOC Removal	-	63%	75%	85%
Color, APHA	820	700	320	170
Color Removal	-	20%	63%	80%

Data represents three months operation of continuous, laboratory 7.5 liter units. Temperature range for all units was 18 to 25°C and hydraulic residence time was 8 hours.

With the "PACT" process, a single piece of equipment, the aerator, is used to destroy most of the organic waste by a relatively inexpensive biological oxidation treatment. Much more expensive carbon adsorption is only used to remove organic compounds which are difficult to biodegrade or completely non-biodegradable. The organic removals achieved in the "PACT" process are greater than the sum of biological oxidation and carbon adsorption removals would predict. This was demonstrated by dosing the effluent from a continuous laboratory activated sludge unit with carbon. The effluent from this batch adsorption treatment had a higher concentration of DOC than the effluent from a parallel continuous "PACT" reactor. There is a synergism in the interaction of carbon and bacteria such that the bacteria are significantly more effective in the presence of carbon than by themselves.

All the design goals for the "PACT" process were achieved in actual plant operation. Table II shows actual WWTP data during the early years of operation when the waste loads were higher.

TABLE II. "PACT SYSTEM" PERFORMANCE
1978 Through 1980

Flow	24,800 GPM
Influent Soluble BOD ₅	175 mg/l (52,100 lbs/day)
Effluent Soluble BOD ₅	7 mg/l
% Removal	96%
Influent DOC	173 mg/l (51,500 lbs/day)
Effluent DOC	32 mg/l
% Removal	82%
Influent Color	1430 APHA
Effluent Color	475 APHA
% Removal	67%
Aerator MLSS (sludge age) 25,000 mg/l (41 Days)	
Carbon Dose	120 mg/l
% Virgin	53%
% Regenerated	47%

Data on average percent removals alone are not the most valid measure of treatment effectiveness. Treatment plants must meet daily maximum as well as monthly average limits, and consistently meeting these daily maxima can be as demanding of a treatment process as meeting a monthly average. The treatment consistency of the "PACT" process has been excellent. Figures 3 and 4 are histograms showing the distribution of feed and effluent concentration for soluble BOD₅ and DOC over a typical operating period for the Chambers Works WWTP. There is a particularly narrow distribution for effluent BOD concentration.

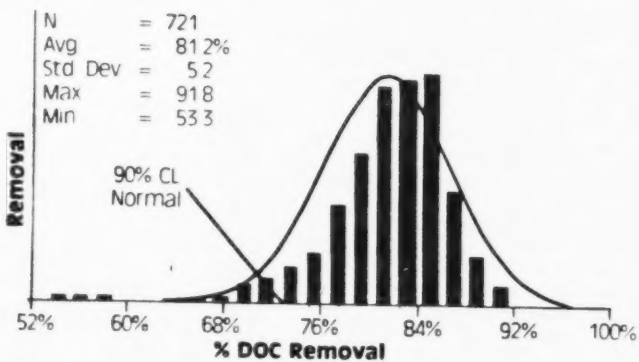
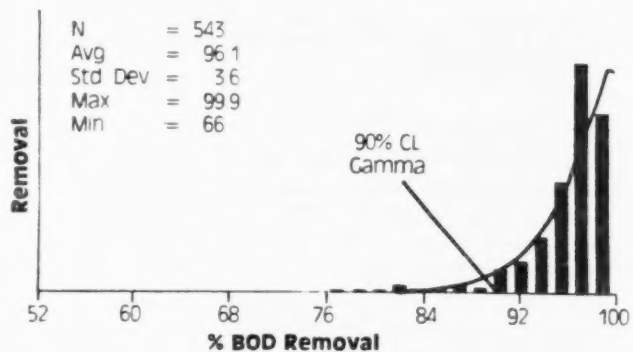
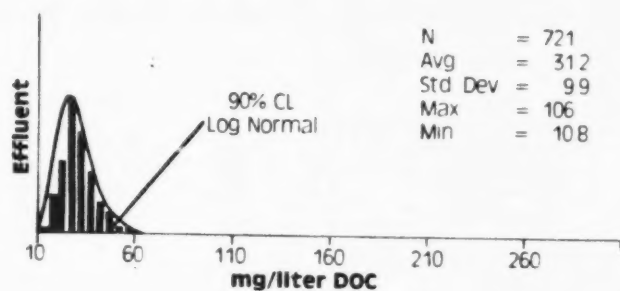
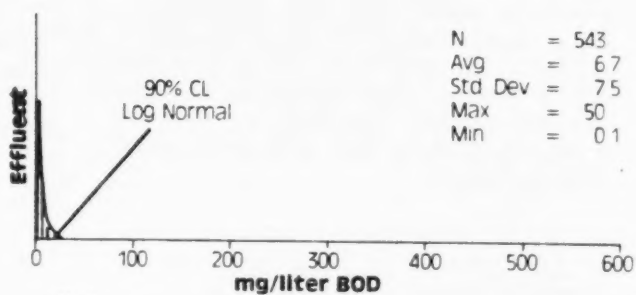
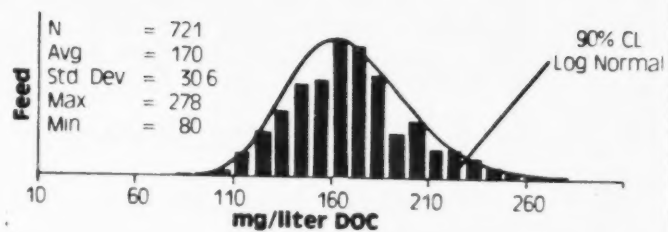
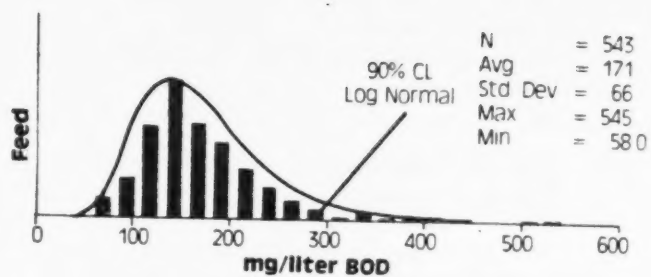


Figure 3. BOD Histogram
('78, '79 Data)

Figure 4. DOC Histogram
('78, '79 Data)

Analytical studies on removal of priority pollutants by the "PACT" process have been made. They generally show the same or greater degree of improvement in removals over an activated sludge process as for conventional pollutants. There are, of course, wide differences in percent removals among specific compounds. Typical data from one study are shown in Table III.

TABLE III. PRIORITY POLLUTANT REMOVALS ACROSS "PACT SYSTEM"

Concentration in ug/liter (ppb)

Compound	Feed	PACT Effluent	% Removal
<u>Volatile Organics*</u>			
Benzene	105	0.9	99
Carbon Tetrachloride	94	1.4	99
Chlorobenzene	1720	30	98
Chloroethane	280	12	96
Chloroform	201	21	90
Ethylbenzene	41	1.7	96
Methyl Chloride	1770	Nil	99
Tetrachloroethylene	24	1.7	93
Toluene	519	1.7	99
1,1,1-Trichloroethane	13	0.6	95
Trichloroethylene	41	1.9	95
Trichlorofluoromethane	155	3.0	98
<u>Base-Neutral Extractables*</u>			
1,2-Dichlorobenzene	259	120	54
2,4-Dinitrotoluene	1900	243	87
2,6-Dinitrotoluene	1640	575	65
Nitrobenzene	454	2	99
1,2,4-Trichlorobenzene	523	169	68
<u>Acid Extractables*</u>			
2-Chlorophenol	11	1.6	85
2,4-Dinitrophenol	161	5.0	97
4-Nitrophenol	1020	10	99
Phenol	489	38	92
<u>Metals</u>			
Antimony	24	24	Nil
Arsenic	19	21	Nil
Beryllium	1.4	1.0	29
Cadmium	5.6	5.4	4
Chromium	26	15	42
Copper	72	75	Nil
Lead	112	54	52
Mercury	.02	.01	50
Nickel	77	59	23
Selenium	29	23	21
Zinc	602	360	40

*The values in Table III are averages of data which show significant day-to-day variations in removals. Results were obtained by GC/MS analyses of plant samples and are subject to analytical error. The figures represent only estimates of average percent removals for these materials.

3) Use of Treatment Plant for Outside Wastes

An obvious possibility with a large WWTP such as the Chambers Works Facility, is using it to treat outside wastes. In the case of Chambers Works this was encouraged by a major reduction in production activity at the site, in particular the ending of dyes manufacture. By the end of 1981 the organic removal capacity of the WWTP was only about 50% utilized.

In an effort to alleviate some of the resultant cost burden on Chambers Works operations, a marketing study was made to see if an outside waste treatment business was viable. It was found that a very large "PACT" plant had some unique advantages.

Because of the large volume of wastewater being treated, the WWTP had essentially an unlimited volumetric capacity for trucked-in aqueous waste. Four tank trucks simultaneously discharging 5,000 gallons each over 20 minutes would increase wastewater flow by less than 5%. Highly acidic wastes could be easily treated. As an example, a 2500 gallon tank/truck of almost 100% waste chlorosulfonic acid has been discharged into the wastewater feed stream in 4 hours with absolutely no fuming problem.

The tremendous dilution provided by over 20,000 gpm flow was a major protection against the organic shock loads that could be caused by a tank truck discharge. Because the WWTP and "PACT" system had been designed to handle large, varying loads of aqueous wastes containing organic materials, the process was ideally suited to treat batch discharges of almost any organic-containing waste, including those that would pass through or be inhibitory to a conventional biological treatment system.

This specific site occasionally has a competitive, quality advantage in treating dilute, aqueous wastes when it is important to the customer that the waste be entirely treated on site, with no residual discharge to the environment or other treatment facility.

The market survey indicated there were significant quantities of aqueous wastes, both at other Du Pont sites and from non-Du Pont facilities that could be treated successfully and on a cost effective basis at Chambers Works. It also turned out to be cost effective to ship wastes substantial distances.

A formal marketing program was established in 1980. Since that time the outside waste business has shown steady growth. Currently over 30% of the organic load to the WWTP is from non-Chambers Works wastes. Over 50% of the waste originates in New Jersey and over 85% comes from the New Jersey, Pennsylvania, Maryland, Delaware region. However, the WWTP has received wastes from as far away as Maine, Ohio, and Georgia. The freight-logical area has been extended in some cases by shipping wastes by rail car, although as yet this is a minor part of the business.

Wastes from a variety of industries have been suitable for treatment. Table IV shows some of the industries now sending significant quantities of aqueous waste to Chambers Works for treatment.

TABLE IV. TYPICAL INDUSTRIAL WASTE-WATERS TREATED AT CHAMBERS WORKS

-
- Tank Truck & Tank Car Washings
 - Pharmaceutical Wastes
 - Water from Oil-Water Separation Processes
 - Textile Treating Wastes
 - Metals Treating Wastes
 - Bio-sludges from Industrial Waste-water Treatment Plants
 - Electronics Industry Waste
 - Landfill Leachates
 - Lagoon Clean-Ups
 - Chemical Process Wastes
 - Latex Wastes
 - Chemical Cleaning Rinse Waters
 - Waste Acids or Bases
 - Food Processing Wastes
 - Paint & Dye Wastes
-

Initially outside waste treatment was limited to dilute, aqueous wastes that could be added directly

to the WWTP inlet waste stream, and whose presence had no significant effect on the quality of the WWTP effluent. A carefully developed outside waste acceptance protocol that includes administrative and analytical check had to be developed to assure the waste could not cause any environmental concerns. Because of the nature of the WWTP there are very few dilute organic wastes that cannot be treated. However the inlet waste stream is acidic, so wastes that generate toxic or noxious gases, such as those containing sulfide or cyanide, cannot be added directly into the inlet stream.

The presence of heavy metals and their removal in primary treatment must also be evaluated, since the Chambers Works NPDES permit has specific discharge limits for a variety of heavy metals. Many heavy metals containing wastes can be satisfactorily treated with careful control of process conditions. No radioactive wastes or wastes characterized as PCB wastes are accepted, nor are those that contain dioxin.

The outside waste treatment has been so successful that Du Pont is expanding the business beyond the capability of the WWTP itself. One proposal is to establish pretreatment facilities that themselves generate aqueous waste streams which the Chambers Works WWTP would then treat. A Du Pont Environmental Services organization has been established to both market the present treatment capabilities of the WWTP as well as develop new environmental business.

Disclaimer

The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Supercritical Extraction of PCB Contaminated Soils

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Supercritical fluid (SCF) extraction of organic hazardous waste from contaminated soils is a promising new technique for hazardous waste site cleanup. The ability of SCFs to solubilize heavy molecular weight organics is well documented. In this investigation supercritical carbon dioxide (SC-CO₂) was used to extract PCBs, DDT, and toxaphene from contaminated topsoils and subsoils. An attractive feature of this process is that the CO₂, being virtually inert, will leave no solvent residue on the processed soil. Furthermore, the ease of separation of the extracted solute from SC-CO₂ results in the creation of a smaller waste volume of the now concentrated organic, improving the efficiency of subsequent treatment processes such as combustion.

Typically in SCF extraction a simple solvent gas, such as carbon dioxide, is contacted with a solid or liquid phase at high pressure and moderate temperature. Slight changes in the temperature or pressure of the system can cause large changes in the density of the solvent and consequently its ability to solubilize heavy non-volatile waste compounds from the solid or liquid phase. For example, by manipulation of the system pressure a non-volatile can be extracted. Following a pressure letdown, generally to below the system's critical conditions, this same material can be completely precipitated from the solvent. Thus the SCF phenomenon offers a unique opportunity for separation and recovery of "difficult to separate" materials in one processing stage.

Supercritical fluid densities compare to liquid densities, however their viscosities and diffusivities are intermediate to those properties for liquids and gases. Thus SCF have the solvent power of liquids with better mass transfer characteristics than typical liquids. Consequently separation efficiencies for SCF extractions can be much higher than for liquid solvent extractions.

An experimental design involving two soil types, a topsoil and a subsoil, contaminated by three organic waste mixtures, PCBs, DDT (and related compounds), and toxaphene was employed to determine the effectiveness of SC-CO₂ extraction. For the first tests the topsoil

was contaminated with approximately 900 ppm of DDT and 400 ppm of toxaphene; this test soil was obtained from an actual spill site where the DDT and toxaphene had penetrated the soil for a period of 10-12 years. For the next tests, the uncontaminated topsoil (from an area near the contaminated soil) was spiked in the laboratory with 600 ppm DDT. In the final tests, the subsoil, spiked with 1000 ppm PCBs (Aroclor 1254), was used. The test soils were supplied by the LSU Wetland Soils and Sedimentation Laboratory.

Several factors affecting soil character also affect extraction efficiencies, and some of these have been explored. For example, the effect of water in the soils was investigated by examining both dry and wet (20% water) test soils. The effect of long-term exposure of the soil to the organic waste was examined via extraction experiments on both spill-site and lab-spiked topsoils. Finally, the effect of solute interactions was explored by testing spill-site soils contaminated with more than one organic waste. Approximately 70% of the DDT and 75% of the toxaphene can be leached in under ten minutes by SC-CO₂ extraction.

The SC-CO₂ extraction of the laboratory contaminated (with PCBs) subsoil proved to be most promising, with over 90% PCB extraction in under one minute.

In addition to the systematic exploration of factors which may affect soil extraction efficiencies, a more fundamental study of the extraction process has recently been undertaken. Desorption equilibrium constants [$k = (\text{fluid phase composition})/(\text{composition in soil})$] have been measured for the various contaminants on the soils in the presence of a SC-CO₂ solvent phase. These equilibrium constants are being used in a lumped parameter model of the extraction process to yield overall mass transfer coefficients characteristic of SCF extraction.

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MICROBIAL DEGRADATION OF POLYCHLORINATED BIPHENYLS

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ABSTRACT

We have used a rapid assay to screen and characterize the polychlorinated biphenyl (PCB) degradative competence of 30 new bacterial strains isolated from diverse PCB-containing soils and sediments. These strains differ widely in the extent, rate, and congener specificity of their PCB degradative activity, and may utilize several different enzymatic pathways. We have defined at least three groups of organisms based on their ability to degrade one or more of the following PCB structural classes: blocked at all 2,3 positions; blocked at 4,4' positions; and lacking adjacent unchlorinated positions. Several of these bacteria degrade penta- and hexachlorobiphenyls. The strains include many *Pseudomonas* and *Alcaligenes* species. We have found major differences in PCB degradative competence among species of the same genus, and some differential competence among strains of the same species. In addition, PCB degrading bacteria have been isolated from every PCB-containing site examined. Metabolic intermediates have been characterized from many of these bacterial strains and suggest the presence of both previously described and novel catabolic enzymes. Current work involves further elucidation of the biochemical and genetic basis for PCB degradative competence, as well as development of technologies which utilize microbial degradative organisms or enzymes.

INTRODUCTION AND PURPOSE

The accumulation of xenobiotic compounds in our environment has had a profound effect on our physical, social, economic and political well-being. Some of these substances have been found to be harmful to humans while others, including PCBs, have only been implicated as such. In either case, there has been a growing demand for their safe disposal or preferably destruction.

More than 100 forms (congeners) of PCBs, differing in the number and posi-

tion of chlorine substituents, were commonly used over the last half-century. The chemical and physical properties which formed the basis for their use (thermal stability, chemical stability) have also contributed to their accumulation in the environment. In addition, they are highly insoluble in water and only slightly mobilized by aqueous systems. Thus, PCBs are generally found in soil and sediments at sites of their production, use, storage or disposal.

PCBs, especially the more highly chlorinated congeners, have generally been considered resistant to biodegra-

dation in the environment. (For a recent review see reference 1). However, new data indicate that both aerobic and anaerobic biotransformations may be much more prevalent than previously thought (2,3). The accumulation of PCBs in the environment and possible effects on human health have sparked an intense interest in devising an economical means for their destruction. It is for these reasons that we have undertaken an extensive study of the microbiology, biochemistry, and molecular genetics of bacteria that degrade PCBs.

APPROACH

Soil and sediment samples were obtained from PCB-contaminated sites in New York, Massachusetts, and California, and a non-PCB containing site in Mississippi. The bacterial populations in these samples were then enriched and analyzed for their ability to degrade PCBs. From these mixed cultures pure cultures were isolated and characterized as to species, substrate utilization, antibiotic resistance, PCB degradative competence (both Aroclors and pure congeners), PCB degradation products (metabolites), regulation of PCB competence, and the presence of plasmids.

Specifically, soil or sediment was added to a phosphate buffered minimal salts medium (PAS) containing biphenyl (BP) or BP plus PCB as sole carbon and energy source. In this way bacteria were selected for their ability to grow on BP. After several passages on PAS/BP the mixed bacterial cultures were assayed for their ability to degrade PCBs. For these assays biphenyl-grown cells were harvested, washed, and resuspended in phosphate buffer at an optical density of 1.0 at 615 nm. One ml aliquots of this cell suspension were dispensed into screw-capped vials. Controls were prepared either by heat-

inactivation of cells at 70°C for 20 minutes, or by addition of HgCl_2 to a final concentration of 1mM. The PCBs (Aroclor 1248 or defined mixtures of pure congeners) were added to a final concentration of 10 ppm, incubated at 30°C with shaking for 24 hours, then killed by the addition of 10 ul of perchloric acid. The acidified cultures were extracted with 2-4 volumes of hexane or ether. Samples were analyzed by gas chromatography on a Varian 6000 gas chromatograph with electron capture detector using either packed column or fused silica capillary techniques. Results for all cultures were calibrated using a non-degradable PCB congener (e.g., 2,4,5,2',4',5'-hexachlorobiphenyl or 2,4,6,2',4'-pentachlorobiphenyl) as internal standard.

Pure cultures were isolated by selection of individual colonies from PAS/agar plates which contained BP as the sole carbon source. These clones were alternately colony purified on PAS/BP/agar and Luria agar plates. All pure strains were initially characterized using the N/F system (Flow Laboratories, Inc.). Selected isolates were sent to the American Type Culture Collection (ATCC; Rockville, MD) for positive identification. The pure cultures were then assayed for their PCB degradative competence as described above. An example of an Aroclor 1248 depletion assay is shown in Figure 1.

For metabolite determination, bacterial cultures were assayed exactly as in the substrate depletion assay except that PCB congeners were analyzed individually and introduced at concentrations ranging from 1-500 ppm. Following incubation for various times the cells were acidified (pH 1-2) and extracted with four volumes of anhydrous ether. An aliquot of the ether phase was then reacted with N_2O -bis (trimethylsilyl) acetamide (BSA, Pierce

Chemical Co., Rockford, IL), then assayed using gas chromatographic analysis as described above.

Six isolates were screened for the presence of plasmids using the procedure of Hansen and Olsen (4). For those cultures where plasmids were detected, the DNA was characterized by agarose electrophoresis and restriction endonuclease analysis.

PROBLEMS ENCOUNTERED

Prior attempts to assay microorganisms for PCB degradative competence by measuring disappearance of Aroclors (commercial PCB mixtures) have frequently produced false positive findings because of volatilization or adsorption losses. Furthermore, these assays have generally left the chemical nature of the competence obscure because of incomplete gas chromatographic resolution and uncertain identification of the Aroclor peaks. We have avoided these problems by using defined mixtures of PCB congeners and by adopting incubation and extraction techniques which prevent physical loss of the PCBs. The assay mixtures include PCBs ranging from dichlorobiphenyls to hexachlorobiphenyls and representing several structural classes: chlorinated on a single ring (2,3-dichlorobiphenyl); blocked at 2,3 sites (2,5,2',5'-tetrachlorobiphenyl); blocked at 3,4 sites (4,4'-dichlorobiphenyl); and lacking adjacent unchlorinated sites (2,4,5,2',4',5'-hexachlorobiphenyl).

Packed column GC analysis of these mixtures following a 24 hour incubation with resting cells permits quantitation of differential congener competence. These studies have allowed us to definitively and unambiguously define the PCB degradative competence of all new isolates. One such assay is shown in Figure 2.

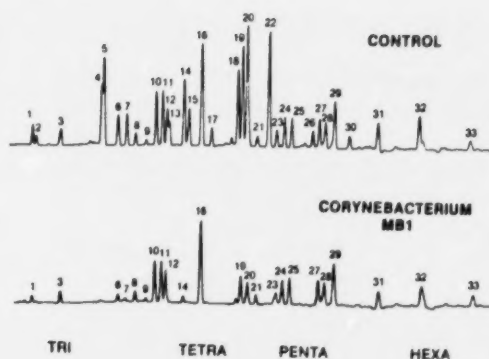


Figure 1. MB1 Degradation of Aroclor 1248 (10 ppm).

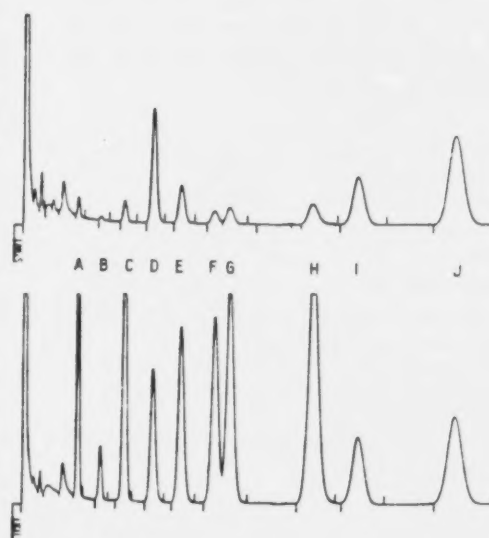


Figure 2. MB1 Degradation of Defined PCB Mixture. Lower GC is control

- | | |
|---------------|--------------------|
| A - 2,4' | F - 2,3,2',3' |
| B - 4,4' | G - 2,4,3',4' |
| C - 2,4,4' | H - 2,4,5,2',3' |
| D - 2,5,2',5' | I - 3,4,3',4' |
| E - 2,3,2',5' | J - 2,4,5,2',4',5' |

RESULTS

PCB Competence of Pure Cultures

We have isolated PCB degrading bacteria which vary considerably. Our isolates (Table 1) include a gram positive *Corynebacterium* species; *Pseudomonas* belonging to three different ribosomal RNA homology groups (*P. putida*, *P. cepacia*, and *P. testosteroni*); an *Alcaligenes faecalis*; and a strain (*A. eutrophus*) formerly assigned to the genus *Alcaligenes* but which in fact probably represents a new genus (5). Our findings illustrate the wide diversity of environmental microorganisms which have developed the ability to degrade PCBs. In the future we would like to determine whether the genes specifying the PCB degradative enzymes in these organisms are related. This information would give us a better understanding of the origin of PCB degradative competence.

<i>Corynebacterium</i> sp.	MB1
<i>Alcaligenes faecalis</i>	Pi434
<i>Alcaligenes eutrophus</i>	H850
<i>Pseudomonas</i> :	
<i>Pseudomonas putida</i>	LB400, LB410
<i>Pseudomonas cepacia</i>	H201, Pi704, RJB
<i>Pseudomonas testosteroni</i>	H128, H336, H430
<i>Pseudomonas</i> sp.	Pi939, H1130
(<i>Acidovorans</i> group)	H702, Pi101

Table 1. Identification of PCB Degrading Bacterial Strains.

Table 2 shows the PCB degradative competence of 26 pure cultures assayed on defined mixtures of 18 PCB congeners. As we had previously seen with the mixed cultures, there is a wide spectrum of degradative competence. When examined in this format, it becomes immediately obvious that there

is a natural progression of degradative capability. The nine strains with the poorest ability to degrade PCBs primarily attack congeners containing a non-chlorinated ring or a ring with a single chlorine in the para position. The remaining strains attacked congeners containing a ring with a single ortho chlorine and showed varying abilities to degrade tetra and pentachlorobiphenyls. These trends in degradative competence may indicate that the PCB degradative enzymes of these strains are closely related. On the other hand, the differences in congener specificity exhibited by strains MB1 and H850 suggest that there are several distinct pathways of PCB degradation. This is discussed more fully in a later section.

Several of our pure cultures easily degrade tetra- and pentachlorobiphenyls. Even more significantly, *P. putida* LB400 attacked every congener in the defined congener assay. Other congeners which are attacked by LB400 include 3,5,3',5'-tetrachlorobiphenyl, 2,4,6,3',5'-pentachlorobiphenyl, and 2,4,5,2',4',5'- and 2,4,6,2',4',6'-hexachlorobiphenyls. It is particularly noteworthy that none of these congeners contain adjacent unchlorinated sites. Possible explanations for this activity are the presence of a monooxygenase or dehalogenase in this bacterium. This would be a novel and extremely important finding in terms of basic bacterial biochemistry and potential decontamination of environmental PCBs.

Our varied collection of bacterial isolates has allowed us to assess whether there is any relationship between the taxonomic classification of a bacterium and its ability to degrade PCBs. The similarities of congener specificity in completely different species suggest that the genes encoding the PCB degradative pathway may reside in diverse populations, possibly on plasmids.

COMMON RING SUBSTITUENT	PCB CONGENER	P1304	P1939	P1434	P1403	H201	P1404	H702	P1442	H1330	P1704	H91	P39	P1101	H9A	E12	P1432	H337	H125	H430	E13	H128	H81	H336	P1918	H850	LB400
	2,3	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
4-	2,4'	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
	4,4'	P	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	P	+	
	2,4,4'		P	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
	2,5,4'						P	+	+	+	+	+	+	+		P	+	+	+	+	+	+	+	+	+	+	
2-	2,2'												+	+	P	+	+	+	+	+	+	+	+	+	+	+	
	2,5,2'											P	P				P	+	P	P	P	P	+	+	+		
2,3-	2,3,2',3'													P	P	+	+	+		+	+	+	+	+	+	+	
	2,3,2',5'																						+	P	+	+	
	2,4,5,2',3'																						+	P	P	P	
2,4- OR 3,4-	2,4,3',4'						P	P						P	+	P	P	P	P	P	P	P	+			P	
	2,4,2',4'																							P	P	+	
	2,5,3',4'																						P		+	+	
	3,4,3',4'																				P	P				P	
2,5-	2,5,2',5'																								+	+	
	2,3,4,2',5'																								+	+	
	2,4,5,2',5'																								+	+	
	2,4,5,2',4',5'																								+	+	

Table 2. PCB Degradative Competence of Pure Strains. P = 20-59%, + = 60-100% Degradation.

PCB Metabolites

Our bacterial strains show a varied yet substantial capability for degrading PCBs as demonstrated by our substrate depletion assays. We have now furthered the biochemical analysis of several of these strains by using a metabolite assay to characterize the products of these bacterial oxidations. The demonstration of metabolic products is important for several reasons. First, it unequivocally confirms that PCB depletion, as demonstrated by our various depletion assays, is due to bacterial oxidation. Second, it allows us to begin to elucidate the metabolic pathway for these oxidations; and third, it shows that more than one pathway for PCB degradation exists in bacteria since different organisms can produce different metabolites from the same PCB congener.

A time course analysis of the metabolites produced from *P. cepacia* H201 incubation with 2,4'-dichlorobiphenyl is depicted Figure 3. The oxidation of 2,4'-dichlorobiphenyl (50 ppm) by H201 is rapid and essentially complete in one day. It results in the accumulation of 2-chlorobenzoate as would be expected from the general observation that bacteria oxidize biphenyl and PCBs via benzoic acid intermediates, and often accumulate the chlorobenzoate products (1). In addition, H201 shows the transient production of a high molecular weight intermediate (Figure 3,B). This presumably is an initial oxidation product (e.g. dihydroxydichlorobiphenyl) which is further degraded to the chlorobenzoate. Our GC-mass spectrometry studies with many other PCBs have indeed shown that the transient high molecular weight intermediates of PCB degradation are hydroxylated-chlorinated biphenyls. The mass spectrum of one such intermediate from the oxidation of 2,3 dichlorobiphenyl by *P. putida* LB400 is depicted in Figure 4.

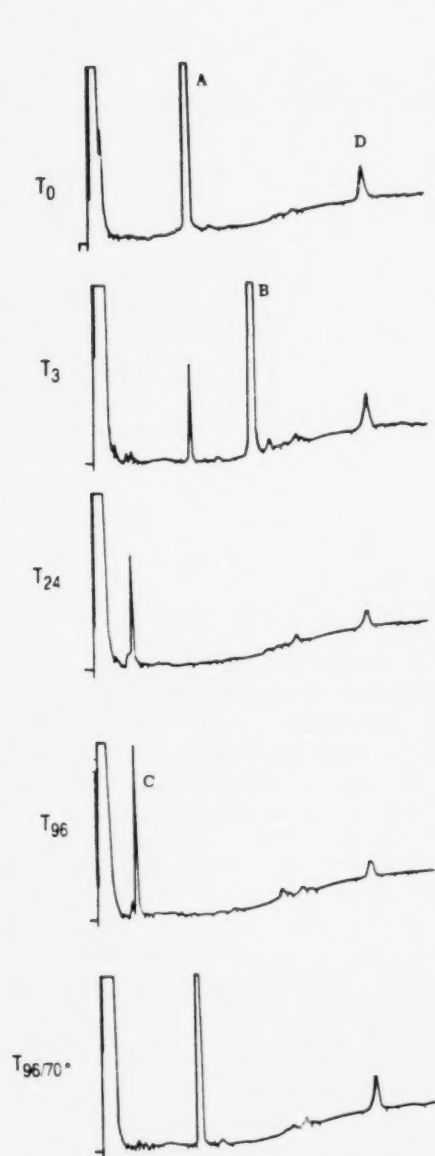


Figure 3. H201 Oxidation of 2,4'-dichlorobiphenyl. Incubation times are indicated at the left. Bottom panel is heat inactivated control. A = 2,4'-CB; B = transient high molecular weight metabolite; C = 2-chlorobenzoic acid; D = internal standard.

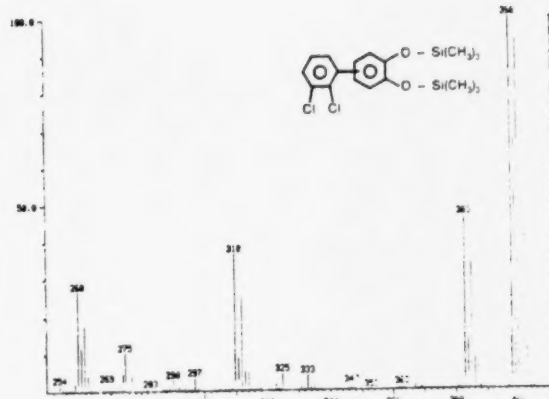


Figure 4. Mass spectrum of a derivatized (trimethyl silyl) metabolite from the LB 400 oxidation of 2,3 dichlorobiphenyl. Determined to be a dihydroxy dichlorobiphenyl.

With the more highly chlorinated PCBs, these high molecular weight intermediates often accumulate. This has helped to facilitate our analysis of the complete PCB degradative pathway. An example of such an oxidation is shown in Figure 5. The parent pentachlorobiphenyl (A) is only partially degraded by LB400 and at 20 hours there appear to be several metabolites (B-D). We are presently characterizing these compounds using GC-mass spectrometry.

PCB Degradative Pathways

A comparison of the PCB competence of *Corynebacterium* sp. MB1 with *A. eutrophus* H850 reveals that MB1 is far superior in its ability to degrade congeners substituted in both para positions. On the other hand, congeners which are chlorinated at positions 2,5,2' are preferentially degraded by H850 (MB1 cannot oxidize 2,5,2',5'-tetrachlorobiphenyl at all). MB1 degraded 4,4'-dichlorobiphenyl almost completely to the 4-chlorobenzo-

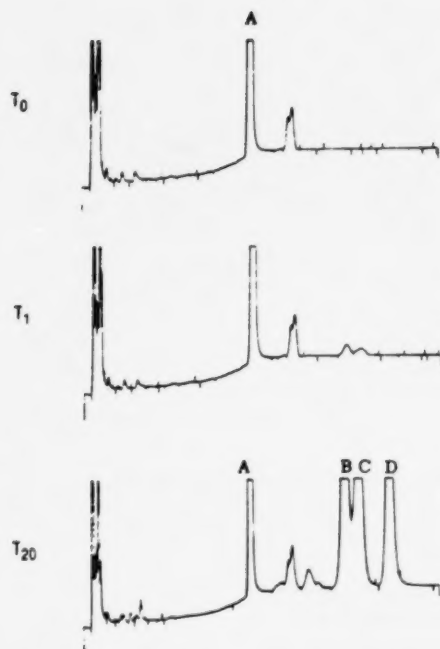


Figure 5. Oxidation of 2,4,5,2',5' penta-chlorobiphenyl (50 ppm) by LB 400 resting cells for 0, 1, and 20 hours. A = 2,4,5,2',5' CB; B-D = high molecular weight metabolites.

ate, whereas H850 shows only poor activity on this congener. These differences are most pronounced at higher PCB concentrations. In addition to exhibiting distinct congener preferences, MB1 and H850 produce different metabolites from the same congener.

Based on these data, we have proposed that the major pathway of PCB metabolism in *A. eutrophus* H850 utilizes a dioxygenase which preferentially attacks at carbon positions 3,4 (6) (Figure 6). If this is the case, it will be the first demonstration of involvement of a 3,4-dioxygenase in the biodegradation of biphenyl or PCBs. In contrast, *Corynebacterium* sp. MB1 probably employs a more common 2,3 dioxygenase mechanism. We are currently in

the process of isolating metabolites from both H850 and MB1 in order to elucidate these degradative pathways.

Genetics of PCB Degrading Bacteria

In addition to our microbiological and biochemical studies of specific PCB degrading bacteria, we have initiated research into the genetic basis for this enzymatic competence. An understanding of the structure and expression of the genes which encode these enzymes will help us to develop superior enzymes, organisms and technologies for the biological destruction of PCBs.

Our initial experiments have involved studies of the endogenous plasmids harbored by several of our PCB degrading bacterial strains. To date, we have demonstrated that at least three of our PCB degrading bacterial strains contain one or more plasmids. Studies with mutants of H850 show that the loss of the ability to utilize biphenyl and metabolize PCBs is sometimes associated with loss of its plasmid. Our goal is to ascertain whether any of the plasmids of H850 and our other PCB-degrading cultures, harbor the genes for biphenyl growth and PCB degradative competence. We hope to transfer this competence, using either transformation or conjugation techniques, to strains of bacteria that are not capable of growth on biphenyl.

This work is preliminary to the eventual isolation of the specific DNA sequences which encode the biphenyl/-PCB degradative enzymes. Ultimately, the cloning and characterization of biphenyl/PCB catabolic genes should lead to a better understanding of the enzymatic oxidation of PCBs as well as a biochemical process for their destruction. It is toward this goal that our genetic research is ultimately directed.

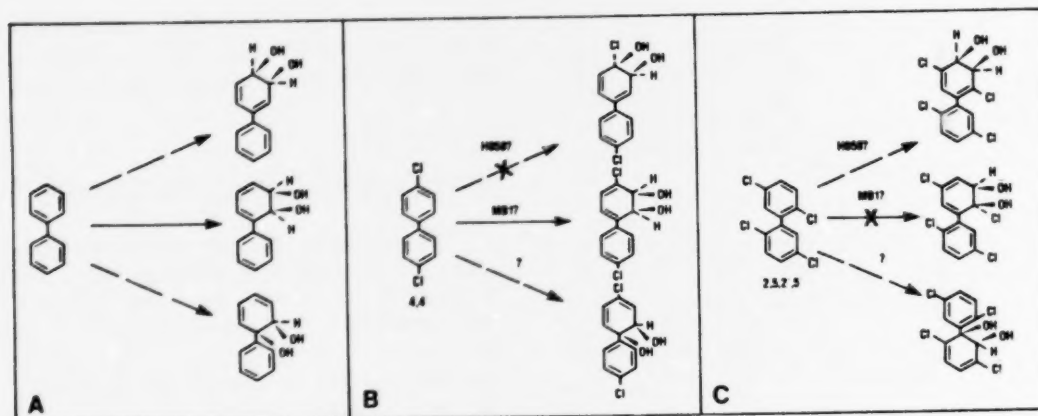


Figure 6. Proposed Initial Oxidation of PCBs by 2,3- and 3,4-dioxygenases.

Disclaimer

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RADIOLYTIC DECHLORINATION OF POLYCHLORINATED BIPHENYLS

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ABSTRACT

Sherman (28) found that, in alkaline isopropanol solutions, some chloro-organic compounds were dechlorinated on exposure to high-energy radiation, via a chain reaction. Later, this work was extended to the polychlorinated biphenyls (PCBs) by Shinozaki and co-workers (24).

We have repeated and extended the work reported by Shinozaki and co-workers and obtained a higher efficiency (G value) for dechlorination. The effects of various inorganic and organic additives on the dechlorination process were also determined. The radiolytic dechlorination process has been used successfully with drained capacitors containing adsorbed PCBs, as well as with soil contaminated with PCBs. Some runs were done on the scale of 20-L solutions. Considerations relevant to the industrial application of this process are discussed.

INTRODUCTION

Increasing concern about the environmental and toxicological effects of halogenated compounds (7,12) led to a ban on the use of one of the more prominent members of this group, the polychlorinated biphenyls (PCBs) (13), in most countries.

Polychlorinated biphenyls are stable and mobile in the environment. They have been found in marine life (14,15), and cases of PCB-contaminated food have been reported (27, 34). The toxicity of PCBs has been the subject of many studies (7,11,12, 15,18,19,27,34,37) and they have been classified as extremely toxic and carcinogenic by the Environmental Protection Agency (U.S.A.), which has placed strict restrictions on their use (20). Similar restrictions have also been imposed in Canada (4).

Almost one hundred methods are available for detoxification, or safe disposal, of PCBs (4). However, most PCBs that have been taken out of service remain in storage. At present, the most widely used method of disposal is incineration (4,6) at temperatures greater than 1100°C. While the process is safe and effective at temperatures > 1100°C (8,16, 17,31), at lower temperatures the destruction of PCBs is incomplete (16), and accompanied by the production of even more toxic compounds, benzofurans (1,3,4). Cases of unsatisfactory incineration of PCBs have been reported by the media. Perhaps, on-line monitoring of the temperature in the combustion zone and of the organic chlorine (in PCBs, dioxins, benzofurans, etc.) in the exhaust gases and ashes needs to be added, or improved, at some of these facilities.

The use of high-energy radiation for the dechlorination of PCBs and other halogenated compounds at ordinary temperatures has been intensively investigated (2,4,9,11,14,22-26,29,32,33,35,36). Since the first report of radiolytic chain decomposition of N_2O -saturated alkaline isopropanol solutions (27), many reports of radiolytic chain reactions in alkaline alcohol solutions have been published (2,5,10,23-25,28-30). The method was then applied to the dechlorination of PCBs by several Japanese investigators (2,23,24,30) who established the following: (i) chain dechlorination of PCBs, with the initial $G(Cl^-) > 600$ (G = number of molecules formed or destroyed per 100 eV of energy absorbed) (31)); (ii) stoichiometric equivalence of the production of chloride, acetone and biphenyl, and the loss of the alkali; (iii) an inverse relationship between $G(Cl^-)$ and the dose rate; (iv) inhibition of the dechlorination by biphenyl, acetone, oxygen and nitrobenzene; (v) stepwise dechlorination of the PCBs.

Shinozaki (6) estimated the cost of the dechlorination of PCBs (~ 54% chlorine) to be 890, 95 and 54 yen/kg, by photolysis, cobalt-60 radiolysis and radiolysis with a 3-MeV accelerator, respectively. (Now, 2 yen equals about \$1 US.) We found this work promising and have reinvestigated and extended it.

EXPERIMENTAL

Experimental details have been published earlier (31). Very briefly, the work was done with Arochlor 1254 (trichlorobenzene removed), drained capacitors and PCB-contaminated soil. The chloride anion yield was determined with ion-specific electrodes and an Orion ion analyzer.

Analyses for PCBs, their radiolytic products, acetone and the cover gas were done with a gas chromatograph (Hewlett-Packard Model 7620A with a flame-ionization detector and an electron-capture detector). The formation of hydrogen and methane was determined by mass spectral analyses; the yields of both of these were very low ($G < 0.5$).

RESULTS AND DISCUSSION

Our results with small (mL) samples of solutions of PCBs in alkaline isopropanol were very similar to those reported by Shinozaki and co-workers (23,24). However, the efficiency of our process is about twice that reported by them. We have optimized conditions to maximize $G(-PCBs)$ -values and have obtained values of $G = 75 \pm 5$ in small samples. For the 20-L runs, the best value for $G(-PCBs)$ obtained so far is 80. In comparison, the values for $G(-PCBs)$ reported by Shinozaki and co-workers (23,24) were < 39 . For capacitors, we have obtained values of $G(-PCBs) \approx 25$.

Irradiation of slurries of PCB-contaminated soil in alkaline isopropanol lead to the dechlorination of PCBs. The yields were, however, lower than for liquid PCBs by factors of two to four, as shown in Table 1.

Table 1. Initial yield (yield extrapolated to time 0) of chloride anions ($G_0(Cl^-)$) on irradiation of 3.3% PCBs in alkaline isopropanol.

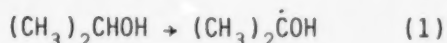
Additives	$G_0(Cl^-)$
None	~ 4000
Clay soil	~ 2300
Top soil	~ 1000

The effect of cationic and anionic additives on radiolytic dechlorination was also examined. The presence of Fe^{3+} , Mg^{2+} , Ca^{2+} , Mn^{2+} , CO_3^{2-} , SO_3^{2-} , SiO_3^{2-} and PO_4^{3-} did not have any effect at concentrations of $10^{-3} \text{ mol} \cdot \text{dm}^{-3}$. While sodium and potassium hydroxide gave similar results, ammonium hydroxide dramatically reduced the dechlorination efficiency. Several organic additives reduced the dechlorination efficiency.

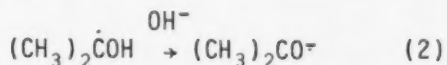
Mechanism

The key reactions that bring about the stepwise dechlorination are as follows:

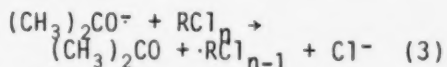
On irradiation, the isopropanol radical is formed.



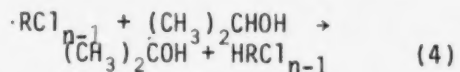
In the presence of alkali, this radical undergoes ionic dissociation to produce the acetone anion.



The acetone anion reacts with PCBs (RC1_n) with charge transfer, which results in the loss of one of the organic chlorine atoms as a chloride anion.



The free radical formed reacts with isopropanol, regenerating the isopropanol radical, and thus propagating the chain reaction.



The detailed mechanism has been discussed elsewhere (31). The ultimate

main products are biphenyl, potassium chloride and acetone.

Advantages of the Radiolytic Process

Some of the advantages of the radiolytic process over the other processes (6) are as follows:

- (1) The process is carried out in the absence of oxygen or air. This completely eliminates the possibility of the formation of benzodifurans or dioxins.
- (2) On-line monitoring of the dechlorination of PCBs is a key component of the process, thus eliminating the possibility of incomplete detoxification.
- (3) The process is applicable to bulk PCBs as well as to PCB-contaminated items.
- (4) The process converts a toxic waste into useful products.

Further Work

We plan to test the efficiency of the process using an electron beam from an electron accelerator for irradiations. Where large quantities of PCBs are stored awaiting disposal, electron accelerators may be cheaper sources of radiation than isotopic sources. Preliminary calculations suggest that irradiation costs with accelerators could be as low as 20¢/kg, for the 10 MeV linear accelerator designed at the Chalk River Nuclear Laboratories by J. McKeown and co-workers (21), provided the efficiency of dechlorination does not change much at the higher dose rates. This figure does not include handling charges, the costs of the chemicals and analytical services, or expenditures for some further research and development required to optimize the irradiation conditions. We are working on a detailed cost analysis for the process. However, one thing is

clear; the cost would be highly dependent on whether the product chemicals, KCl, acetone and biphenyl, can be marketed. We are also working on details of detoxifying transformers and large amounts of contaminated soil.

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U.S. DEPARTMENT OF DEFENSE MANAGEMENT OF HAZARDOUS WASTE

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ABSTRACT

The U.S. Department of Defense (DoD), as a large buyer of hazardous materials and a large generator of hazardous wastes, is concerned with the management and disposal of increasing quantities of hazardous wastes.

Each DoD installation is required to comply with the requirements of federal environmental laws and the 50 states' and many local solid and hazardous waste laws and regulations. The Office of the Secretary of Defense develops the policy and monitors the overall programs results of the DoD components - the Army, Navy and Air Force. The Defense Logistics Agency (DLA) has the central responsibility for DoD hazardous waste disposal.

The DoD hazardous waste site cleanup program encompasses a systematic effort to cleanup inactive or abandoned DoD hazardous waste sites. The Department is making a strong effort to coordinate its programs with all levels of government and to keep the public informed concerning the problems and progress being made.

New waste management operations will significantly reduce the production of hazardous wastes. Methods include: reduction in the amount of hazardous materials used, substitution of less hazardous materials, better quality control, applications of innovative technology, and recycling.

INTRODUCTION AND PURPOSE

The Department of Defense (DoD), the purchaser of more than 50,000 hazardous material line items each year ranging from paint removers to pesticides, adhesives to fuels, and propellants to industrial solvents, has a cradle-to-grave chemical waste management program as mandated by Public Law 94-580, the Resource Conservation and Recovery Act of 1976 (RCRA) and Public Law 94-469, the Toxic Substances Control Act of 1976 (TSCA).

DoD generated an approximately 92,000 metric tons of hazardous wastes in 1981, while the United States generated about 57 million metric tons

of hazardous waste in the same year (6). The DoD wastes are by-products of its operations and manufacturing processes, specifically, explosive and propellant manufacturers, as well as high technology for specialized military applications.

Most DoD waste streams are similar to the civilian sector's in terms of the industrial activities generating wastes as shown in Table 1.

This paper describes and analyzes DoD's hazardous waste management and its research and development programs.

Table 1

MILITARY HAZARDOUS WASTE STREAMS

<u>Base Industrial-Related Operations/Process</u>	<u>Hazardous Wastes</u>
Metal finishing	Acids Heavy metals Caustics
Degreasing	Solvents [e.g., trichloroethylene, methyl ketone (MEK)]
Painting and stripping	Paint strippers and thinner Waste epoxy (resin)
Miscellaneous aircraft repair wastes	Brake relining wastes (beryllium) Metal stress and defense analysis wastes (fluorescent dye) Welding wastes (acetylene sludge)
Fuel storage and supply operations	Fuel and oil wastes Tank bottom sediment Tank cleaning sludges
Pest control shops	Waste pesticides Equipment wash water
Battery shops	Battery acids Alkaline battery fluid

Hazardous Waste Cleanup Programs

DoD's hazardous waste program encompasses identification, control, and cleanup of inactive or abandoned disposal sites (Installation Restoration (IR) Program), and management of hazardous waste from current and future operations.

DoD started its IR program in 1975, five years before the passage of CERCLA, commonly known as "superfund". Under CERCLA, Section 103(c), notifications of all known or suspected closed hazardous waste sites were to be made to EPA by June 1981. Although 82 percent (227 or 274) of DoD installations reporting in response to Section 103(c) were already included in the IR program, some were not. This was because individual DoD installations frequently reported suspected sites based only on scant knowledge in order to err on the side of safety. While evaluation of these sites is still in progress, almost all sites reported under Section 103(c) and not previously included in the IR program have been confirmed as not to require any follow-on action.

The Department's goal is to complete records searches to identify hazardous material sites potentially requiring corrective actions at every installation likely to have hazardous material problems by October 1985. The Deputy Assistant Secretary of Defense for Installations monitors the progress of the military departments toward this goal.

Three hundred ninety DoD installations require records searches. One hundred ninety-four have been completed to date. The remainder will be finished by September 1985. DoD estimates that searches cost approximately \$50,000 each. To date, remedial actions have been started at ten installations.

Probably the most widely reported DoD installation restoration project is the Army's effort at Rocky Mountain Arsenal, Colorado. Rocky Mountain Arsenal is adjacent to the City of Denver, with Stapleton International Airport lying directly south of the Arsenal. The Arsenal complex, some 17,000 acres, has groundwater contamination resulting from military chemical warfare agent production and Shell Chemical commercial pesticide production. The Army's project at Rocky Mountain Arsenal began in 1976. To date, over \$45 million has been spent to define contaminant migration and provide remedial actions at the Arsenal.

The data collection and analytical effort at the Arsenal has been extensive. Over 1,500 wells have been drilled on the 25 square mile site. Four to six thousand analyses are completed every month, with over 270,000 data points on record and over 900 technical reports published. The Army has demonstrated at Rocky Mountain Arsenal the commitment of the Defense Department to pursue its cleanup of old waste sites.

Installation Restoration Research and Development

The Army is the lead service for compiling, refining and coordinating the development of new and improved technology and criteria for DoD IR Program. As part of this lead service responsibility, the Army chairs a Tri-Service Technology Coordinating Committee. At the present time, the Army has three interagency agreements with Environmental Protection Agency (EPA) involving research and development for better hazardous waste management. The Air Force and EPA are presently developing an additional agreement. The objective of these agreements is to ensure cooperation and coordination between DoD and EPA in research and development for pollution abatement and environmental quality management.

The research efforts include work in the following areas:

- o Decontamination and Cleanup Technology

The thrust of this effort is to identify and develop cost effective technology for hazard containment and soil, groundwater or facility decontamination. The effort includes pilot testing of rotary kiln incineration as an environmentally safe and cost effective method for disposing of waste lagoon sediments,

studies of effectiveness of barrier and liner materials for containing hazardous materials, basic study of encapsulation and fixation techniques for isolating materials, study and evaluation of techniques for removal of contaminants from groundwater and lagoon wastewater including carbon absorption, polymeric resins, and supercritical fluid methods. Nondestructive methods for cleaning-up buildings and facilities contaminated with explosive, organics and heavy metals are also under study and evaluation. The successful containment/decontamination system currently employed at the north boundary at Rocky Mountain Arsenal to prevent migration of contaminated groundwater across the boundary was an outgrowth of this R&D program.

Under its research and development program, the Defense Department is developing innovative as well as conventional methods to resolve hazardous waste decontamination problems. DoD installations and Defense Logistics Agency (DLA) are pursuing actively these alternative solutions. The continuously increasing costs for incineration and secure landfills provide the greatest incentive to seek more cost-effective treatment and disposal technologies. DoD supported the first major project for ocean incineration of toxic chemical wastes when the Vulcanus was outfitted to dispose of remaining supplies of herbicide orange. Molten salt combustion, composting, deepwell disposal, and soil incorporation (land farming) are all currently under investigation by DoD.

A cooperative project is currently planned at the Louisiana Army Ammunition Plant located near Shreveport, Louisiana, to demonstrate closure technology for industrial waste lagoons.

The closure of the first waste lagoon was completed in FY 83 using solidification of lagoon sludges and in-place burial. Technology for closure of another, which contains chemicals from explosive manufacture, is still under study.

o Criteria Development

This effort includes environmental effects studies of contaminants found at DoD installations which are not typical problems for the civil sector. These efforts will help establish meaningful decontamination and health hazard potential criteria. Vegetative and wildlife studies are being performed on the compounds identified during the assessment phases of the IR program. Since the inception of the IR program, over 20 compounds and their decomposition products have been studied. Currently, studies are underway on dioxin, hydrazines, urea, picrates, and picramates. The latter two compounds were found contaminating the soil at a Naval installation.

o Analytical Systems

The Defense Department found early in the IR program that standardized analytical methods and sample reference materials were required. To promote consistency and reliability of results, analyses were performed by various government and contractor laboratories. Over 200 analytical procedures and 60 standard analytical reference materials traceable to the National Bureau of Standards have been developed for the IR program. The analytical procedures and methods provide the basis for DoD IR program quality control procedures.

Management of Hazardous Wastes from Current and Future Operations

The Defense Property Disposal Service (DPDS) of the Defense Logistics Agency has storage and disposal responsibility for all hazardous materials turned in to DPDS by the Army, Navy, and Air Force for disposal. Since mid-1980 the DPDS has had a central responsibility to assure that DoD hazardous wastes are disposed of in accordance with Federal, state, and local laws and regulations.

These materials are disposed of either on-site or by contract agents, again in conformance with applicable federal, state, and local laws and regulations.

DoD policy is that the DIA's hazardous materials disposal cycle must include an evaluation of waste material salvage and resale possibilities; i.e., recycle of materials. An example of DIA's recycle approach was in the recent sale of 368 tons phosgene (manufactured as a chemical warfare agent by the Army during World War I) to a civilian firm in New York State. The firm used the chemical (carbonyl chloride) as a feedstock for urethane plastic manufacture.

In two other important areas, studies recently completed have shown that bases using only a few drums of solvent per year can economically recycle these materials using commercially available stills. DoD is now developing a comprehensive program for waste solvent segregation collection, distillation, and recycling. In the related area of waste lubricating oil, the Department is investigating re-refining at regional centers for recycle to DoD users.

Collection, storage, and disposal of DoD's toxic and hazardous materials are accomplished through 142 Defense Property Disposal Offices located on military installations throughout the world, and 74 additional off-installation branches, which serve as collection, storage,

and transfer points. DPDS's normally dispose of materials by contract to commercial firms. Contract preparation is handled either at Defense Property Disposal Service Headquarters in Battle Creek, Michigan, or at one of their five Defense Disposal Regional Offices.

DoD has many of its own storage treatment and disposal facilities across the nation, but it relies primarily on civilian contract firms for treatment or ultimate disposal of hazardous waste. In 1981, DoD disposed of 51,000 tons on its own sites and 127,000 tons off its installation (4).

Reliance on outside firms is critical to DoD. The United States needs about 50 to 60 new hazardous waste management sites over the next several years (7).

Compounding the problem is the fact that hundreds of old, environmentally inadequate disposal sites are scheduled for remedial action requiring removal and relocation of wastes. Other existing facilities will be forced to close as strict RCRA regulations go into effect or as they reach their capacity. Unfortunately, many recent attempts to locate sites for new facilities have not been successful because of opposition from local residents. Few new off-site hazardous waste treatment or disposal facilities have been sited in the United States since 1978 (1,5). Florini suggested interstate compacts for hazardous waste management similar to those being developed for low-level radioactive waste (2), under the Low-Level Radioactive waste Policy Act of 1980.

The Army is developing new and innovative technology for more effective management of hazardous wastes and materials at its industrial facilities and training and readiness installations. Research thrusts include development of technology for control of wastewater and air emissions from munitions plants and depots, development of environmentally safe disposal techniques for obsolete or excess munitions, recovery and reuse of explosives and propellants and development of computer aided systems for effective management of hazardous materials at Army installations. Development of a sulfide precipitation method for treatment of electroplating waste was recently completed and a pilot system installed at Tobyhanna Army Depot for operational evaluation.

Other examples of Defense programs to resolve hazardous waste problems are the Navy chrome recycling effort and Air Force programs for air stripping of solvents from groundwater and recovery of paint stripping solvents.

The Naval Air Rework Facility (NARF), Pensacola, Florida, was selected as the test site for a joint Navy-Department of Energy test of closed-loop system for recycling toxic chrome electro-plating wastes. The project involves an energy efficient evaporation concept which concentrates hazardous waste effluents to a point where they may be returned to the electroplating process, thereby conserving resources and avoiding hazardous waste generation. Initial results have been very promising, and there is additional work underway to apply the concept to other electroplating processes such as cadmiumcyanide. The potential is considerable, and the Navy is considering installation of the process at other chrome electro-plating facilities.

The clean-up of contaminated groundwater via packed tower air stripping and reclamation of paint stripping solutions are two Air Force projects with potential broad application. Trichlorethylene (TCE), an organic solvent previously used by numerous DoD and commercial activities as a degreasing agent, has been discovered at various concentrations in groundwater aquifers throughout the United States. The Air Force's Engineering and Services Laboratory, located at Tyndall Air Force Base, Florida, has been studying packed-tower air stripping for its efficiency and economic soundness as a method for handling long-term clean-up of TCE in groundwater. Packed tower air stripping is a process involving stripping of volatile impurities (TCE) in liquids by exposure of the contaminated liquid to a turbulent countercurrent air stream. The impurities are stripped from the liquid by transfer to the air which is subsequently exhausted. Since TCE concentrations are often very low, less than one part per million, air emissions are not likely to be significant. If they are important, carbon absorbers may be added to the system. Even this dual treatment system is likely to be cost effective because the life of the carbon absorbers is much greater when treating air streams than when treating water streams. The feasibility of air stripping other volatiles is also being studied.

The paint stripping solvent reclamation project is directed toward developing new methods to extend the life of paint stripping solutions. Deterioration in paint stripper performance coincides with the buildup of paint solids. Laboratory testing at the Air Force

Engineering and Service Center established techniques to remove the paint solids from the stripping solution and the recovered product met performance specifications. A full-scale precoat, pressure filtration system has been installed at Hill Air Force Base, Utah, and is being evaluated. Successful operation of the filtration process will save \$50,000 for every month the life of the paint stripper is extended. This project is an excellent example of reducing waste quantity by material reuse.

The Army has formalized coordination of its research efforts with EPA under a memorandum of understanding and the Air Force and EPA developed a similar agreement. The Army agreement has the objective of promoting cooperation and coordination of research in hazardous materials and other areas and establishes a committee to monitor and promote coordination efforts.

FINDING AND RECOMMENDATIONS

The DoD hazardous waste site cleanup program encompasses a systematic effort to cleanup inactive or abandoned DoD hazardous waste site. DoD is making effort to coordinate its programs with all levels of government and to keep the public informed concerning the problems and progress being made.

New waste management operations will significantly reduce the production of hazardous wastes. Methods include: reduction in the amount of hazardous materials used, substitution of less hazardous materials, better quality control, applications of innovative technology, and recycling.

The use of these methods will not necessarily eliminate the waste problem. However, waste generation control can greatly alleviate the total waste volume and degree of hazard in many military operations.

Hazardous waste source generation control should be incorporated as an integral part of the overall military hazardous waste management program. Installation activities should be examined by base and technical support personnel to determine feasible source reduction operations and reuse incentives.

High hazardous waste disposal costs necessitate a new emphasis in several phases of the military system including procurement, manufacturing, maintenance, and refurbishing operations. Economic analyses can not be limited to research and development, acquisition, and operation and maintenance costs but should include the projected costs and benefits of hazardous waste management. For example, the material acquisition system should include the costs of handling and disposing of any hazardous material safely and analyzing any hazardous waste recycling or reuse potential (3).

DoD management is also concerned with technology development for cleanup operations and hazardous waste reduction and is working with EPA in cooperative research and development efforts in these areas.

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CHARTING THE COURSE TO ENHANCED SOURCE REDUCTION

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ABSTRACT

The report by the National Academy of Science Committee on Institutional Considerations in Reducing the Generation of Hazardous Industrial Waste examines key institutional, or nontechnical, factors that affect the generation of hazardous waste by industry. It provides a framework for evaluating public policies, both regulatory and nonregulatory, to reduce the generation of hazardous waste. The report does not itself provide clear-cut solutions; rather, it provides a foundation upon which improved public policies for hazardous waste management can be built.

The report's underlying premise is that waste reduction should be an integral component of any national waste management strategy. For the purposes of this report, "waste reduction" refers not only to in-plant process modifications that reduce the volume and/or degree of hazard of hazardous waste generated, but also to reuse and recycling practices.

This report is the first to deal with non-technical factors affecting the generation of industrial hazardous waste. Because little study has been devoted to this topic, committee members have relied on their own experience and judgment in formulating their recommendations. The committee hopes to stimulate public discussion of this subject as an important component of hazardous waste management.

INTRODUCTION

To some it may have seemed like just another tough assignment for the National Academy of Science. However waste reduction studies can be intensely emotional, fueled by the fires of partisan politics

and scientific skepticism. The final report by the "Committee on Institutional Considerations in Reducing the Generation of Hazardous Industrial Wastes" is history now. It will have to stand on its own merits for those who read it and attempt to utilize its recommendations in initiating or improving waste reduction programs. This paper will outline some of the struggles which lay behind this document.

* The views expressed are those of the author and do not reflect on those held by his fellow committee members or the National Academy of Science.

The National Academy of Science was chartered by Congress in 1863, i.e., in Abraham Lincoln's days. It was established as a private, nonprofit, self-governing

membership corporation. In 1916 the National Research Council was added to the charter for the purpose of associating the broad community of science and technology with the Academy's purpose of furthering knowledge and of advising the federal government. The Council has become the principal operating agency of both the National Academy of Sciences and the National Academy of Engineering in the conduct of their services to the government, the public, and the scientific and engineering communities.

The Committee on Institutional Considerations in Reducing the Generation of Hazardous Industrial Wastes was organized in September 1983 to explore the nontechnical factors that influence decisions by industrial management to reduce the generation of hazardous waste. The committee, sponsored by the Andrew W. Mellon Foundation and National Academy of Sciences Endowment Funds, was asked to examine the public policy approaches that may lead industries to reduce generation of hazardous waste.

The committee was comprised of the following people:

RAYMOND C. LOEHR, Cornell University (Chairman)

WILLIAM M. EICHBAUM, Maryland Department of Health and Mental Hygiene

ANTHONY O. FACCIOLE, JR., Alexandria Metal Finishers, Inc. (deceased)

SAMUEL GUSMAN, Taos, New Mexico

ROBERT A. LEONE, Harvard University

MICHAEL R. OVERCASH, North

Carolina State University

PHILIP A. PALMER, E.I. duPont de Nemours and Co.

STEFFEN W. PLEHN, Fred C. Hart Associates, Inc.

ROBERT B. POJASEK, Chas. T. Main, Inc.

MICHAEL E. STREM, Strem Chemical, Inc.

Staff

RUTH S. DEFRIES, Staff Officer

PAUL SCHUMANN, NRC Fellow

JOYCE E. FOWLER, Administrative Secretary

The premise underlying the study is that reduction in the quantities of hazardous wastes which are generated and need to be treated or disposed is a benefit to society. The study's goal was not to provide clear-cut solutions to a complex issue; rather, it is hoped that this report will provide a foundation for public discussion from which improved public policies for hazardous waste management can be developed.

Among the "institutional", or non-technical factors the committee considered were economic factors, such as capital costs of waste reduction equipment; regulatory factors, such as stringency of standards; and psychological factors, such as attitudes toward changes.

APPROACH

Waste reduction is a topic which almost everyone is talking about. The committee sought to collect as much information as possible that existed on the subject. This was done in three ways. First an intern was retained to

catalog and summarize the vast amount of information which had been collected by the author on the topic of waste reduction. A literature search was undertaken and groups active in waste reduction were contacted directly to see if there was more recent unpublished information. Second, the Academy staff sent out hundreds of letters requesting input into our process. Many people and groups availed themselves of the opportunity to participate. Several state governors personally responded. Third, the Committee invited guests to its monthly meetings to brief the Committee further on programs currently in progress. These guests included the Massachusetts Department of Environmental Management, Office of Technology Assessment, and representatives of the California, Minnesota, Illinois, North Carolina and New York waste reduction programs. Throughout this intensive search and the numerous appeals directed to industry, very little quantitative, independently verified, and peer-reviewed information was gathered on this topic. Indeed, this was the first attempt at a comprehensive work on institutional considerations.

Many examples of achievements in waste reduction were brought to the committee's attention, and the committee tried to learn what it could from them. It is difficult to generalize, however, from a series of examples where there are limited data to suggest their wider applicability. Much of the report therefore represents the personal experience and considered judgement of the committee.

By the third monthly meeting, the Committee had a draft report to work with. New information and the wide range of Committee members

experience were used to revise the material. Because it was difficult to get a clear picture of exactly what was meant by the term "institutional considerations" in our charter, we opted to utilize a more fundamental "barrier" approach. A large number of barriers to waste reduction were formulated along with the possible means to overcome these barriers. The Committee then decided it could go no further with the available information and that we had something that was potentially ready for release.

To test this judgement, the committee organized a workshop in May 1984 at which a group of highly experienced people from industry, state and federal government, and environmental groups were asked to discuss the issues raised in this report. Discussion papers prepared by the Committee were circulated in advance and served as the focus of the interaction. The papers discussed the institutional barriers to more effective waste reduction in the United States. The workshop participants responded that to focus on the barriers to waste reduction seemed unnecessarily negative, in that it did not highlight the achievements that have been made with waste reduction and wrongly implied that opportunities for waste reduction are limited. The committee then framed the ideas in this report in a more neutral tone, focusing on "factors affecting industrial decisions about waste generation".

A digest has been prepared to provide widespread, immediate, free dissemination of the core of the committee's deliberations to policy makers in all sectors, industrial leaders, and others who are concerned with means to reduce the generation of hazardous industrial waste. The full committee report, Reducing Hazardous Waste Generation: An Evaluation and Call for Action, priced at \$4.95 list, is available from the National Academy Press at 2101 Constitution Avenue, Washington, DC 20418. The present format of the Report is outlined in Table 1.

TABLE 1. NATIONAL ACADEMY OF SCIENCE
REPORT OUTLINE ON REDUCING
HAZARDOUS WASTE GENERATION

Summary of Analysis and Conclusions

1. Introduction
 - Scope of the Study
 - Definitions of Hazardous Waste
 - Estimates of Hazardous Waste Generation
 - The Role of Waste Reduction in Waste Management Strategies
 - Dynamics of Waste Reduction Strategies
2. Factors Affecting Industrial Decisions About Hazardous Waste Generation
 - Introduction
 - Cost of Land Disposal
 - Attitudes Toward Change
 - Availability of Information About Waste Reduction Methodologies
 - Regulatory Issues in Reducing the Generation of Hazardous Waste
 - Needs for Research and Development
 - Capital Costs
 - Issues in Assembling, Processing, and Sale of Recycled Materials
 - Product Quality Standards
3. Approaches for Encouraging Hazardous Waste Reduction
 - Approaches for Encouraging Firms to Reduce Hazardous Waste Generation in the Initial Phase
 - Approaches for Encouraging Firms to Continue Waste Reduction Programs in the Development Phase
 - Considerations in the Mature Phase

References

Appendixes

- A Hazardous Waste Management Methodologies
- B A Typical Waste Reduction Program
- C Additional Documents Reviewed by the Committee
- D List of Workshop Participants
- E Biographical Sketches of Committee Members

PROBLEMS ENCOUNTERED

There were some definitional problems at the start. The term "waste reduction" as used in the report, refers not only to in-plant process modifications that reduce the volume or degree of hazard of the hazardous waste generated, but also to the reuse and recycling of hazardous materials. These later cases can be accomplished both on and off the site of generation. Many state waste reduction programs have chosen to exclude off site activities in their programs or not distinguish between recycle and reuse.

Industrial decisions about waste reduction are made for varied and complex reasons. The committee's task to understand these reasons was constrained by the lack of data on waste generation and by the lack of extensive literature on the nontechnical aspects of waste reduction. Therefore many of the observations and conclusions in the report are based on the collective experience of the committee members. The members bring a broad spectrum of experiences to the committee, from large and small firms, public administration at the federal and state levels, and consultancy with industry.

The report was reviewed by an outside group of experts under the Academy's strict peer review guidelines. The committee is required to respond to all the comments. A report review committee consisting of members of the Academy is assigned to review the committee's responses.

A generally polar response pattern was evident in the comments as shown below:

"The report does not impress me. To the contrary, it leaves me uninterested."

"Overall, the draft is clear, organized and useful as a general treatment of the subject. It is balanced and contains numerous practical insights."

"My first impression was the feeling this was basically a philosophical or policy document but with little meat to it."

"It is a comprehensive document that proposes a complex solution to reducing our nation's hazardous waste management requirements."

This will provide some indication of the degree of opinionation that can develop in such a new, yet politically active area. As the data base increases and we are able to gain a better understanding of what is happening and why, this diversity of opinion should be less polar. Certainly there will be more reports. Such a worthy goal as waste reduction demands more than just the "talk" it has been receiving to date.

RESULTS

As a result of its deliberations, the committee arrived at the following general principles that should govern efforts to reduce the generation of hazardous waste.

No single approach to encouraging waste reduction will be most effective in all circumstances.

The effectiveness depends on variables, such as the type and size of the industry or plant and the amount of waste reduction that has already been achieved. The dynamic character of waste reduction programs provides a framework to explore the potential effectiveness of public policy alternatives.

Reductions in the generation of hazardous waste can be expected to occur through a series of loosely defined and overlapping phases. Initially, firms consider changing their current waste management practices in order to exploit technically simple, low-cost waste reduction opportunities. Firms then undertake increasingly sophisticated, more costly technologies to achieve further waste reduction. Finally, firms begin to confront the political, economic, and technical limits to waste reduction activities. Different public policies are appropriate at different stages of an industry's waste reduction effort.

It is desirable to reduce the generation of hazardous waste. Regulatory standards, however, should be based on overall health and environmental considerations and not made more stringent than necessary solely to encourage waste reduction. If properly developed and applied, standards will be a strong impetus to undertaking waste reduction efforts.

The costs of alternative methods of waste disposal should reflect the social costs of protecting public health and the environment. The incentive for industrial firms to pursue opportunities for reducing waste generation will be inadequate if the disposal option remains priced below the true costs.

Regulation will continue to play a crucial and central role in the overall waste management effort, but future waste reduction is more likely to be forested by non-regulatory methods, such as information dissemination

programs and economic incentives.

CONCLUSIONS

Most waste reduction efforts in U.S. industry are still in their early stages. Many opportunities exist for reducing the generation of hazardous waste. Efforts should begin now to encourage industries to take advantage of these opportunities.

At the current stage of development of industrial waste management programs across the nation, substantial progress in reducing the amount of hazardous waste generated can be achieved by employing relatively simple methods that entail modest capital expense. Such methods emphasize engineering or plant specific circumstances. The amount of waste generation that can be avoided is, unfortunately, not known, because of difficulties in obtaining reliable data.

The current trend toward increasing costs of land disposal for hazardous wastes -- through greater liability for generators and site operators as well as through restrictions on this use of land -- is an extremely important impetus to implementing waste reduction programs. To encourage reduction in the amount of waste generated in the future, this trend bringing the cost of land disposal to the level of its true costs to society should continue.

An important impediment to implementing low-cost waste reduction practices is lack of access to information about them. Developing means to exchange and disseminate information about successful waste reduction projects is an essential first step toward reducing future

waste generation.

Approaches other than the direct regulation of manufacturing processes are needed. Within the regulatory framework, regulations would be beneficial that are administered consistently and predictably and are flexible enough to encourage the use of methods that reduce the generation of hazardous waste.

In the long term, as implementation of newer, more capital-intensive technology becomes necessary to reduce waste generation further, public policies will need to adapt to the different considerations. Industry may require assistance -- in the form of incentives or subsidies, for example -- to help defray R&D as well as capital costs. Risk assessment and risk management studies will be needed for assessments of more sophisticated waste reduction options. Research on these topics should begin now.

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HAZARDOUS WASTE MANAGEMENT STRATEGY IN ILLINOIS: GOVERNMENT'S ROLE

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ABSTRACT

Government can play a valuable advocacy role in the development of a reasonable hazardous waste management strategy within its jurisdiction. State government bodies, in particular, are in a position to stimulate the adoption of waste reduction, resource recovery and alternative treatment practices, as well as to discourage the continued use of land disposal waste management options.

The experience in Illinois clearly demonstrates that the Department of Energy and Natural Resources, as a nonregulatory agency, is a good venue for the promotion of safer waste management options. A balanced program of research, information transfer and industrial assistance has been established to coordinate the development of a statewide hazardous waste management policy. Industrial, academic and public interest groups are involved as contributors to this effort which supplements ongoing activities on hazardous waste problem solving in other states and at federal institutions. The states must recognize that they can assume a waste treatment information transfer role which federal agencies have deemphasized in the past ten years.

INTRODUCTION AND PURPOSE

The development of a comprehensive hazardous waste (HW) management strategy for an entire state is an ambitious undertaking. There are numerous groups with decidedly parochial interests involved in the research, regulatory and enforcement aspects of strategy development which must be

consulted at various stages. Complexities involved in the issues of equitable waste regulation, adoption of alternative technologies to land disposal, information transfer and problem assessment research are all potential obstacles to the development of sound policies for waste management. Regardless of the approach taken by various

governments, hazardous waste management strategy must be approached from a basis of sound information on waste management practices.

Illinois, as a major industrial state with a significant agricultural economic component may provide a suitable model for the development of reasoned waste management strategy for other states. There are definite advantages which result from allowing a comprehensive and consistent technical approach to drive policy development in specific areas of hazardous waste management as contrasted with a confining regulatory approach. A degree of flexibility must be incorporated into the development of an initial strategy to allow for the discovery of new data or waste management market reactions. Clearly, a nonregulatory agency with neutral technically sound response capabilities has an edge in bringing together the diverse societal elements of waste management solutions. Public interest groups, industry and various levels of government share both the cause and solution to hazardous waste management problems if they can be brought together and work cooperatively.

In July 1984, the Governor and the legislature took action to create a group which would provide technical support towards the development of a comprehensive statewide hazardous waste management strategy. The purpose of the program was to provide a balanced program of research, information transfer and technical assistance to industry in Illinois in support of a statewide HW management strategy. This paper describes the early development of the

Illinois Hazardous Waste Research and Information Center (HWRIC). It emphasizes the technical obstacles to hazardous waste problem assessment activities in a major industrial state which may be useful to other government bodies. Industrial and public interest groups may also find the results useful as they face similar challenges in other states.

APPROACH

The initial approach to the development of the HWRIC concept was the transformation of a variety of research and technical assistance activities into a balanced program which would meet the long-term hazardous waste management needs of the State. The experiences of a number of scientists and engineers involved in: ground-water, water and wastewater, geological and toxicological research (in support of regulatory programs) could be summed up as being fragmented and lacking a constituency for necessary long-term support and product implementation. It was clear that legislative and regulatory time-frames were shrinking in response to Federal actions and the public recognition of the seriousness of waste management issues. Further, these time-frames were not synchronized with research agendas dictated by external funding arrangements or priorities. Problems of scale and the basic geographic and climatic differences between the states, which were provided essentially the same Federal fiscal and technical support, placed additional pressure on the state's regulatory agencies as they worked to respond to a number of waste management planning needs. In summary, the

principal outcomes of scientific and administrative task forces (6,7,8,12) were the need for carefully directed research, information transfer and industrial assistance activities in support of a comprehensive hazardous waste management strategy (5). It is reasonable to state that if the technical solutions to various waste management problems could be identified, necessary administrative and regulatory adjustments could be made for effective policy implementation.

RESEARCH

Research activities are frequently undertaken to provide answers to deceptively simple questions of a basic nature. Hazardous waste management issues entail the study of a diverse array of interrelated questions, many of which have no simple, obvious answers. It was obvious that waste problems relate to the properties of the materials involved, where they were generated, transported, treated or disposed and the opportunities for their release or exposure in the environment. It was also obvious that no single scientific discipline could approach unilaterally the solution to the problems of a major industrial state and that Federal research priorities were not necessarily those most critical to our unique situation. In order to focus the limited technical resources available to investigate the symptoms of improper waste management, the research activities of HWRIC were planned in two main areas: problem assessment and problem solving.

Problem assessment research activities were needed to provide

a clearer picture of the extent and magnitude of hazardous waste problems in the state. The need was complicated by the overlapping definitions of hazardous substances covered by various regulations or by hazardous characteristics (e.g. ignitability, corrosivity, toxicity and reactivity). The dimensions of these activities had to be broadened in view of the fact that hazardous wastes had been managed by a variety of means for over 50 years in an environment which may take decades to display symptoms of waste-related impacts. Available regulatory information was limited in waste composition data and the short (i.e. 3-5 year) annual reporting period required that the initial problem assessment efforts were planned as pilot projects. There had been at least three efforts to assess the statewide HW problem in Illinois prior to 1982 (8,9,10,11). These studies had established several important points:

- ◎ There was sufficient overlap between the reporting in the special and hazardous waste categories to discourage generalizations as to major HW generating industries, problem regions or major disposal practices;
- ◎ Deep-well injection and disposal, in or on the land, were major disposal practices for both treated and untreated waste streams; and
- ◎ Estimates of both the total quantity of HW generated and that accounted for by treatment, storage or disposal facilities showed large discrepancies owing to one or more of the following factors:

unspecified on-site practices, accounting difficulties with existing manifest systems and changing economic conditions.

Figure 1 depicts the envelope of estimates for the annual amounts of hazardous waste generated in Illinois from 1920 to 1981 from a variety of sources (2). The estimated quantities were derived from state information, as well as from extrapolations on industrial growth and Illinois' contribution to total U.S. industrial output. Recent generation estimates varied widely and at least half of the total waste generated prior to 1975 was managed in the absence of regulatory controls.

The need for pilot projects for problem assessment was recognized in a number of areas, including: estimation of the potential health risk to human populations via ground water, development of a methodology for searching historical records of industrial and commercial activity and identification of major liquid HW streams, disposal practices and options for their treatment and disposal other than landfilling. The regulatory data has improved in the last two years and an expanded research program is currently underway. The following discussion provides a capsule summary of selected initial research efforts.

Potential Risk via Ground Water

Ground-water contamination may occur by a number of mechanisms. Inappropriate waste management practices have been identified as major potential sources. A study of the

assessment of past sources of hazardous waste related activity in both a rural and urban county provided some very useful insights into the magnitude of the problems which may affect shallow sand and gravel aquifers in areas of high and moderate HW related activity. The counties selected were among the top ten in generation and disposal of manifested RCRA waste streams. A simple HW activity ranking scheme was developed (Fig. 2) and applied in an attempt to screen potentially serious situations towards prioritizing more in-depth investigations. The susceptibility of aquifers to surface contamination based on geologic considerations was supplemented by the development of time-related capture zones for public water supply wells. This approach acknowledges the dynamics of ground-water systems and has been applied to the zoning of industrial/commercial sites in Europe. An example of a time-related capture zone for a well finished in shallow sand and gravel is shown in Figure 3. The 18-month study led to several useful conclusions.

- ⊙ The accuracy and completeness of regulatory data on the generators, waste composition and quantities was frequently suspect because of critical data base management considerations.
- ⊙ Past HW handling activities prevent an equal and perhaps more serious threat to ground-water quality than the more recent data would indicate.
- ⊙ Historical documentation of past waste generation and management practices is

contained in a diverse array of chamber of commerce, county census, property records and trade publications. The most reliable searching methodologies require the expertise of an experienced industrial geographer and considerable manpower.

- ⊙ The ranking scheme had to be limited to planning applications since much of the available data to support its use was incomplete. Risk assessment is a very complex, information intensive discipline (1).
- ⊙ Illinois counties with more than 20,000 gallons (83 tons) of RCRA manifested wastes need more detailed study. This set would include 42 of 102 counties and account for >99% of the total quantity manifested in 1982.

Figures 4 and 5 provide a graphic illustration of the areas which were judged to have degrees of potential risk after application of the ranking scheme in county and metropolitan areas, respectively.

Liquid Waste Characteristics and Management Options

Legislative bans on the land-filling of HW streams have been established in a number of states. In 1982 several related actions were being discussed in Illinois which ultimately lead to a ban on untreated liquid waste landfilling in 1984. The final action encouraged pretreatment but retained an emphasis on free liquids and particularly those associated with organic solvents. Anticipating

the enactment of the ban, an assessment of major liquid waste generation and off-site management alternatives was initiated in a three-county metropolitan area (4). The major findings of this study were:

- ⊙ In 1982, industries in Cook, DuPage, and Lake Counties in the Chicago area generated an estimated total of over 34 million gallons of liquid hazardous wastes that were managed off-site. Cook County generated nearly 90 percent of the total (over 30 million gallons) whereas DuPage County generated the least, at less than 2 percent (about 550,000 gallons). The three counties contributed nearly half of the total state generation of liquid hazardous wastes manifested for off-site management.
- ⊙ Land disposed liquid hazardous wastes managed off-site in the three-county area in 1982 were estimated at nearly 22 million gallons. 12.5 million gallons of this total are generated in the three-county area. Most of the remainder is from industry outside of the area (some from outside Illinois).
- ⊙ Acidic wastes and alkaline wastes were far greater than other waste categories generated. Other major waste generation categories include: paint, solvents, distillation residues, plating, and metal wastes, hydrocarbons, and wastes within a miscellaneous category. The most prominent land disposed waste category is alkaline wastes--with an even greater quantity land disposed than generated.

- ⑥ The results of the waste stream evaluations suggested that feasible waste management alternatives exist for large quantities of liquid hazardous wastes currently being land disposed. Estimated quantities of off-site managed liquid hazardous wastes which could be managed alternatively, were estimated at 12.5 million gallons.
- ⑦ The time required to effect the potentially feasible reductions in land disposed hazardous waste is unknown. Some reductions from the 1982 quantities have already been noted. In addition, the cost for land disposal of hazardous wastes is expected to continue increasing above inflationary levels. The cost effectiveness of alternatives to land disposal was expected to become more evident.

The results of these and several ongoing projects have established a basis for more detailed, statewide HW problem assessment research. We certainly have a long way to go towards a comprehensive waste management strategy.

Problem solving research activities have yet to begin but we are working towards the elements of a ground-water protection plan with the fifteen or more agencies with jurisdiction in this area.

Information Transfer

As a government agency with no regulatory or enforcement responsibilities, ENR has adopted a neutral, technically based

advocacy role in promoting HWRIC's main goals. The reception from the public, state agencies and industry has been encouraging. These diverse interests agree that the emphasis of HWRIC programs should be on the development of high quality technical products which deal with the most critical problems which face the state. As the information base and our understanding improve, we expect to be an active contributor to the development of reasonable waste reduction and management alternatives. We are committed to the free exchange of our research accomplishments (as well as recognized difficulties) with all related efforts.

Industrial and Technical Assistance

The ultimate usefulness of HW research activities can only be realized if the products and understanding gained are eventually applied. A number of states (i.e. California, New York) have initiated industrial assistance efforts towards waste reduction as exemplified by North Carolina's "Pollution Prevention Pays" program (3). Alternative technologies to land-based disposal and end-of-pipe treatments are being developed around the country for application to HW problems. HWRIC's industrial and technical assistance efforts have been planned to supplement these efforts for specific applications to high-risk, high volume waste streams and to support site remediation activities. Cooperative relationships with other state and industry programs have been initiated to insure that economic and environmentally sound practices are considered in future

regulatory and administrative actions.

RESULTS

The beginning efforts of Illinois government towards the development of a comprehensive waste management strategy hold promise for the future. The dimensions of hazardous waste problems are imposing and involve the cooperation of all sectors of society. We intend to share our results with all interested parties in the hope that tractable solutions to these problems can be identified and implemented.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the time, effort and cooperation of ENR staff, their contractors and the staff of the Illinois Environmental Protection Agency. The valued advice and consultation of representatives of industry, state government and the public have been most helpful in the development of these activities.

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Disclaimer

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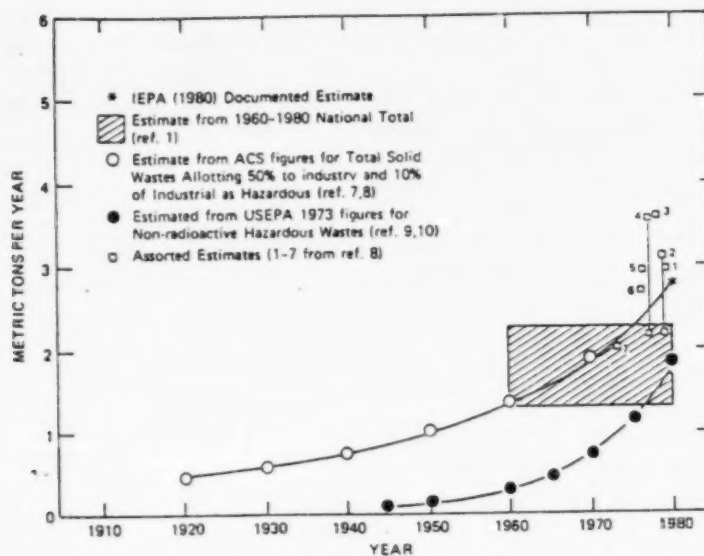


Figure 1. Estimated hazardous waste generation in Illinois 1920-1980



Figure 2. Schematic diagram of ranking factors, values, and input data

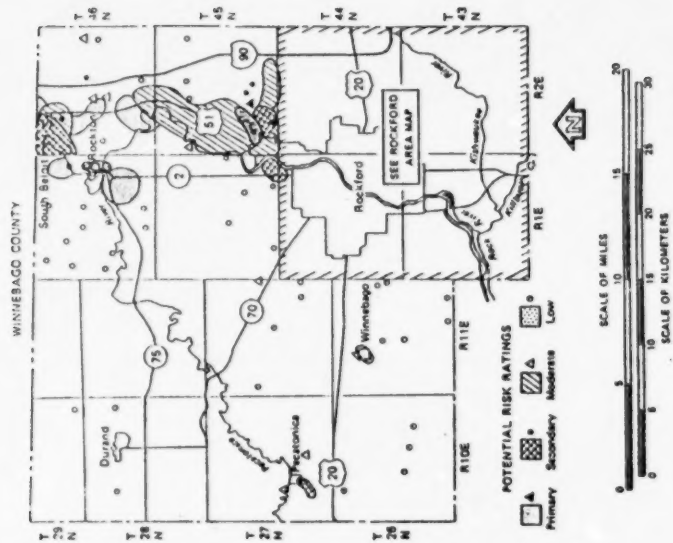


Figure 4. Potential hazardous waste problem areas in Winnebago County

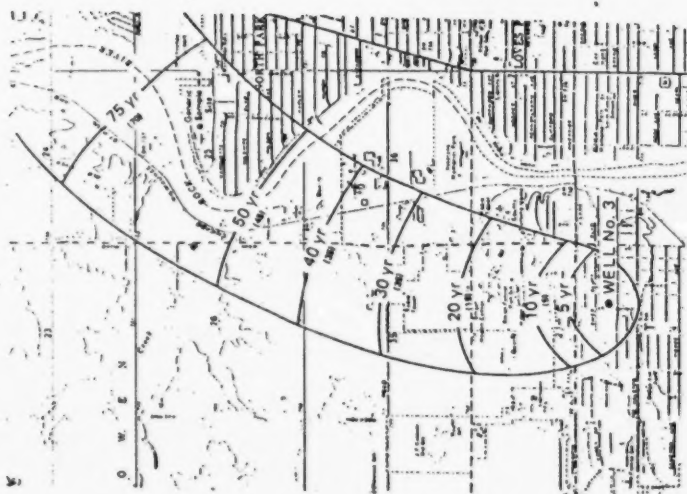


Figure 3. Diagram of a capture area with horizontal travel times (bracketed number) and vertical travel times added (unbracketed number)

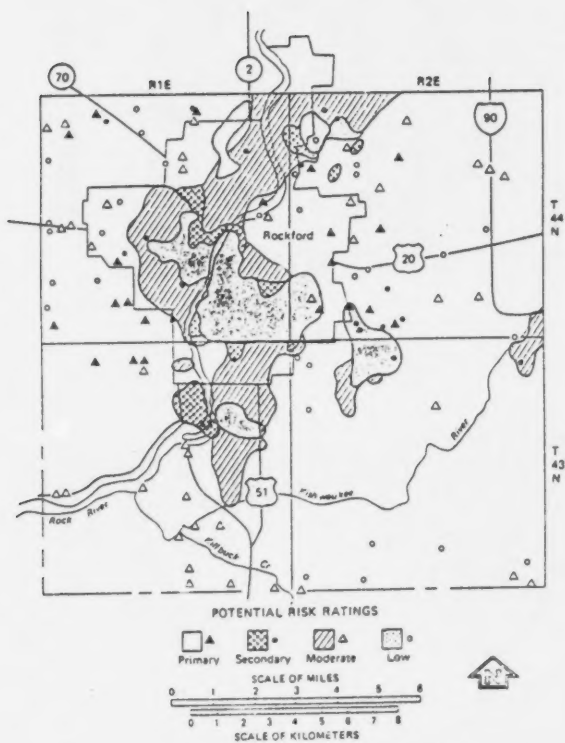


Figure 5. Potential hazardous waste problem areas in the Rockford metropolitan area

EMERGING TOXIC ISSUES FOR THE ELECTRIC UTILITY INDUSTRY

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ABSTRACT

The issue of toxic materials has been the driving force from the very beginning of environmental regulations, because of public concern about wastes in the air, the water, or the land. While regulations still tie public and environmental health to those hazardous substances found in air, water, and land, there has been an evolution in the basic rules of regulations, application of control, and monitoring.

Observation of contaminants is no longer strictly a matter of seeing, tasting, or smelling a problem. The tools of science have moved us orders of magnitude lower in what man can perceive. As technology progresses, the targets for measurement become smaller and smaller. Some regulations seem to have shrinking targets, even as companies are trying to comply, such as the target for PCB spill clean-up. While 50 ppm was once considered reasonable for regulating PCBs, numbers such as 0.05 ppm or whatever is decided to be the detection limit are considered now for clean-up standards. Sometimes that number is vague because of the "no-threshold" level for cancer, where any molecule may potentially lead to an increase in mortality rate.

When the target was larger, it was easier to detect compliance or non-compliance and, therefore, easier to attribute effects to the substance being controlled. Likewise a regulatory standard was something which, if met, absolved one of consequences concomitant with the standard.

That is another change to which companies must adjust. You can meet every permit requirement and be consistent with every legal limitation, but still be liable for the consequences and remedial action if it is subsequently observed that something in your waste is causing harm or even if it is one of a number of potential causes of a victim's ailments. This means that past practices are not things to be forgotten and everyone does not start with a clean slate as new regulations are promulgated. It means that today's best technology may not be good enough when human health and the environment are at stake.

The importance of monitoring is not just in proving compliance to regulators, but of increasing importance, as a warning to you that your system may have a flaw. The sooner the environmental problem is discovered, the cheaper the remedial effort. The responsibility and liability continue as long as the waste has a potential to cause harm.

The regulatory picture is changing also with such concepts as workers right-to-know, toxic torts, and victim's compensation. More information must be collected for companies about the chemicals in use, in both large and small quantities, and about chemicals formerly used.

In some cases the data is sparse or non-existent about the toxicology, health effects, modes of transport, or rates of migration. As processes are developed, the question must be asked, is there a variation which will yield less of a toxic waste or chemicals in less mobile forms. The data base must continually be expanded since the responsibility lasts forever.

What are some of the problems which the utility industry must face? Some that I foresee are the PCB-contaminated sites, town gas disposal sites, regulated underground storage tanks, and pesticides/herbicides usage.

PCB or polychlorinated biphenyl has been a leader in the toxics area. It is the only compound which was specifically called out for regulation in the Toxic Substances Control Act. It has been driven by public fear despite toxicological data. Special handling, disposal, transportation, and recordkeeping are required for this family of compounds.

Utilities, are not discovering new problems from the residues of past practices, which are unsatisfactory by today's standards. Wastehaulers and metal salvagers who took askarel transformers and PCB fluids and mismanaged them have created some contaminated sites. Utilities because of past practices may have created some themselves. In both cases, as these sites are discovered, and finding them even if you are seeking them is not easy without records, utilities can find themselves in the midst of costly clean-up efforts. As stated previously, liability continues, and the financial responsibility finds its way back to the deepest pockets -- the utilities.

Another residual of past practices is the problem of town gas disposal sites. From the late 1800's to about 1950, a major source of residential gas was pyrolysis/combustion of coal. Coal tar was a by-product which was landfilled as a waste product when it was not a salable commodity. Polynuclear aromatic hydrocarbons (PAHs) from the coal tars are on the list of troublesome organic compounds. Cyanide evolved from the organic nitrogen and was scrubbed out by iron oxide, producing ferri- and ferrocyanides. As residuals from pre-1950, it is not only difficult to ascertain what was buried where, but also to find people in the companies who know anything about the operation and disposal procedures. This is another expensive remedial activity. EPA has performed an historical investigation and turned up a list of about 1500 companies who made town gas. Most are extinct companies. Remedial action options are few and not without drawback. Excavation and landfilling may be establishing next year's clean-up problem.

Regulated underground storage tanks (RUST) is not something which one would necessarily associate with the utility industry, but there are a lot of tanks, mainly for storing gasoline. Again, this is a major clean-up problem with few alternatives.

Herbicides/pesticides occasionally receive headlines when tied to foods. Utilities have used these chemicals in and around their facilities and along rights-of-way. Results of storage and utilization potentially can lead to another toxic clean-up problem.

There are new rules for regulation and compliance, and these lead to new problems from old practices. Utilities could find themselves involved in significant toxic clean-up activities in the coming decade.

THE EPA HAZARDOUS WASTE ENGINEERING RESEARCH LABORATORY'S
RESEARCH PROGRAM IN SUPPORT OF SUPERFUND

by

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ABSTRACT

In anticipation of the passage of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA or Superfund), the Office of Research and Development of the USEPA began a program in 1980 to support the Agency's activities concerned with uncontrolled hazardous waste sites. In the area of environmental engineering and technology, the Agency looked to the ongoing and established programs in land disposal of hazardous waste and hazardous spill cleanup. Thus a research program was established to develop and evaluate removal and remedial cleanup technology. This program is now housed in the Hazardous Waste Engineering Research Laboratory in Cincinnati, Ohio.

The Superfund program has been organized into four research areas: (1) containment technologies for remedial actions; (2) on-site cleanup equipment; (3) in-situ treatment of hazardous waste/contaminated soils; and (4) personnel protection.

The containment technologies area includes projects dealing with barriers to minimize surface water infiltration, limit or divert groundwater contact with waste, and control leachate migration; waste storage, either temporary or long-term; waste and leachate treatment; remedial action technical evaluations and modeling; and post closure evaluations.

An analysis of in-situ methods for cleaning contaminated soils has identified three approaches to the problem. The first approach is the extraction of contaminants from the soil with ultimate treatment of the extracted material in conventional wastewater treatment plants either on or off site. Methods such as surfactant washing and freezing would fall into this category. A second approach is the immobilization of the contamination within the soil column and thus eliminating its transport. Included in this approach would be methods such as grouting, pH adjustment, and thermal fusion. The third approach would be the degradation/detoxification of the contaminants in place, for example, the application of microbes or chemicals to the soil that chemically change the contaminants to a nontoxic or less toxic form.

Crosscutting these three approaches is the need for methods to deliver the chemicals, grouts, microbes, etc., to the soil and methods to recover material where applicable.

On-site separation, concentration, and detoxification technologies are an alternative to containment and off-site disposal. On-site technologies being evaluated include a mobile incinerator, soils washer, and carbon regenerator.

The objectives under the personnel protection area are: (1) to develop and evaluate chemical protective clothing and equipment; and (2) to develop and evaluate procedures that will result in reduced chemical exposures, safer working conditions, and more economical and efficient working conditions without a reduction in safety.

In order to transfer the state-of-the-art being evaluated within this program to the user community, a series of Superfund remedial/removal criteria handbooks has been prepared. Following is a listing of the twenty-five handbooks that have been or will be published through FY'86.

1. Guidance Manual for Minimizing Pollutions from Waste Disposal Sites, EPA 600/2-78-142
2. Compatibility of Grouts with Hazardous Wastes, EPA 600/2-84-015
3. Review of In-Place Treatment Techniques for Contaminated Surface Soils,
Volume 1--Technical Evaluation, EPA 540/2-84-003a
Volume 2--Background Information for In-Situ Treatment, EPA 540/2-84-003b
4. Handbook for Remedial Action at Waste Disposal Sites, EPA 625/6-82-006
5. Handbook for Evaluating Remedial Action Technology Plans, EPA 600/2-83-076
6. Slurry Trench Construction for Pollution Migration Control, EPA 540/2-84-001
7. Remedial Response at Hazardous Waste Sites,
Summary Report--EPA 540/2-84-002a
Case Studies--EPA 540/2-84-002b
8. Design and Development of a Hazardous Waste Reactivity Testing Protocol, EPA 600/2-84-057
9. Leachate Plume Management, (to be published in FY'85)
10. Modeling Remedial Actions at Uncontrolled Hazardous Waste Sites, EPA 540/2-85-001

11. Costs of Remedial Actions at Uncontrolled Hazardous Waste Sites: Worker Health and Safety Considerations, (to be published in FY'85)
12. Guide for Decontaminating Buildings, Structures and Equipment at Superfund Sites,
EPA 600/2-85-028
13. Evaluation of Systems to Accelerate the Stabilization of Waste Piles and Deposits, (to be published in FY'85)
14. Covers for Uncontrolled Hazardous Waste Sites, (to be published in FY'85)
15. Stabilization/Solidification Alternatives for Remedial Action at Uncontrolled Waste Sites, (to be published in FY'85)
16. Fugitive Dust Control at Hazardous Waste Sites, (to be published in FY'85)
17. Field Manual for Plunging Water Jet Use in Oil Spill Cleanup,
EPA 600/2-84-045
18. Guidance Manual on Overtopping Control Techniques for Hazardous Waste Impoundments, (to be published in FY'85)
19. A Guidance Manual for the Selection and Use of Sorbents for Liquid Hazardous Substance Releases, (to be published in FY'85)
20. Drum Handling Practices at Hazardous Waste Sites, (to be published in FY'85)
21. Manual of Practice for Marine Safety Officers and On-Scene Coordinators Involved in Chemically-and/or Biologically-Contaminated Underwater Operations, (to be published in FY'86)
22. Manual for Preventing Spills of Hazardous Substances at Fixed Facilities, (to be published in FY'86)
23. Reference Manual of Countermeasures for Hazardous Substance Releases, (to be published in FY'86)
24. Environmental Emergency Control Handbook for Hazardous Substances, (to be published in FY'86)
25. Flammable Hazardous Substances Emergency Response Handbook: Control and Safety Procedures, (to be published in FY'86)

Ordering information for published reports is available from the USEPA, Center for Environmental Research Information, Cincinnati, OH 45268, (513) 684-7562 or (FTS) 684-7562.

Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

SURROGATE COMPOUNDS AS INDICATORS OF HAZARDOUS WASTE INCINERATOR PERFORMANCE

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ABSTRACT

Evaluation of hazardous waste incinerators for Resource Conservation and Recovery Act permits is a difficult and sometimes costly task. The Environmental Protection Agency is evaluating, in its research program, several chemical compounds which may be used to monitor incinerator destruction and removal efficiency and combustion conditions more effectively. This paper discusses the research aimed at developing reliable and cost-effective methods for trial burns, and permit compliance monitoring.

INTRODUCTION

Regulations promulgated under the Resource Conservation and Recovery Act (RCRA) have identified nearly 400 compounds [17] which, if present in a waste material, can cause it to be designated as a hazardous waste and be subject to the rigorous disposal requirements required by law. When wastes containing any of these compounds are incinerated, the regulations require that the major waste components (called principal organic hazardous constituents or POHCs) be destroyed and/or removed to at least 99.99% (destruction and removal efficiency or DRE). Hazardous waste streams are often extremely complex mixtures containing hundreds of compounds of various chemical classes. An analysis for POHC's and other major waste components on a continuing basis is a difficult, time consuming and expensive task.

Since 1979, the Hazardous Waste Engineering Research Laboratory of the USEPA has been intensively involved in research to assess the capabilities of incineration facilities to meet the RCRA standards. This research is currently directed toward identification of easily-monitored facility operating parameters which correlate with, or are surrogates for, system per-

formance. From these efforts, we anticipate establishing a sound scientific basis for the selection of monitoring methods which would simplify and reduce costs of incinerator facility validations and permit compliance monitoring.

BACKGROUND

Much of the attention in thermal destruction research has centered on the incineration of chlorinated organic compounds. Of all the compounds listed as components of hazardous waste, chlorinated organics were given high research priority because they are the most common compounds found in waste and represent a large portion of incinerable wastes generated [11].

Because of the large number of these compounds efforts were initiated early in the research program to reduce the number under study to a manageable level. By selecting POHC's representative of the compounds most prevalent in priority waste categories and which were generated in largest amounts, twenty-eight compounds were initially selected for the research program [11].

A major element in HWERL's thermal destruction research program was to com-

are the relative performance of different types of incinerators, industrial boilers and kilns by means of conducting research trial burns to evaluate DRE. It readily became apparent, in the beginning of this program, that waste analysis and stack sampling was more complex and costly than expected. To simplify research trial burns and to keep sampling and analysis costs in line with the research program budgets, nine of the twenty-eight compounds were chosen for full scale evaluation tests in industrial boilers and processes and pilot scale research. These compounds are listed in Table 1. To be selected, the compounds had to meet the following criteria:

- easily detectable in stack emissions with existing Sampling and Analysis methods
- have high thermal stability for its chemical class
- representative of physical and chemical properties of priority wastes.

Table 1

Compounds Selected for EPA Research Program

carbon tetrachloride
methylene chloride
trichloroethylene
perchloroethylene
chlorobenzene
hexachlorobenzene
pyridine
acetonitrile
toluene

SURROGATES FOR HYDROCARBONS AND HALOCARBONS

After initial field tests, it became apparent that (1) these compounds were not always present in wastes at the sites that were available for testing; (2) there were analytical problems using existing methods with methylene chloride, toluene, acetonitrile and pyridine. The solution to the first problem, was to "spike" or add a known amount of the desired compounds to the waste in order to measure destruction and removal efficiency (DRE). This approach, for the most part, worked well, except that other problems

appeared, such as handling problems due to toxicity, lack of commercial availability and high cost of the spiked compounds. Because of the need for spiking compounds into the waste, and the problems just discussed, it was decided to choose compounds that minimized these problems. Additional selection criteria were added and were made more restrictive by requiring the compounds be [11, 18]:

- non-inflammable
- non-toxic
- commercially available at relative low cost
- high thermal stability
- not likely to be formed as a PIC (Product of Incomplete Combustion)

A group of compounds that fit these criteria are the FREONS, halogenated organic compounds which are commercially available. Table 2 lists some of the more common ones which fit the selection criteria and would simulate a range of POHC physical properties. At a workshop on surrogate's sponsored by the California Air Resources Board [12], Freon 113 was selected as the most promising of those on the list. Its volatility is low, it is miscible with most of the wastes under study, and is low in toxicity. Its chief use is as a degreasing solvent.

The incineration of FREON 113 has also been studied in Sweden, both in incinerators [2] and cement kilns [1]. The Swedish studies reported it to be easy to detect but difficult to destroy. Because of the ease of detection, destruction efficiencies could be determined to a very high degree.

Table 2

Trial Burn Surrogates

Compound	Boiling Point, °C
Freon 11	24
Freon 113	48
Freon 114	4
Freon 2281	150

Since 1983, the USEPA has conducted five research trial burn tests to evaluate the feasibility of using Freon 113 as a surrogate for wastes; three of the tests were at cement plants, one at a lightweight aggregate production plant and the

fifth was at a facility processing montmorillonite clay. Table 3 summarizes the DRE results for each of the processes studied.

The DRE's of Freon 113 and the POHC's in the cement kiln and aggregate plants exceeded the incinerator standards of 99.99% DRE. In the test of the plant processing montmorillonite, Freon 113 was the only halogenated compound present at a significant concentration (>1000 ppm). Even though the process temperature was low, the DRE of Freon 113 was greater than 99.99% throughout the test. The results demonstrate that Freon 113 is as difficult to incinerate as other POHC's in the tests and that it could feasibly be used as a reliable surrogate for most wastes with volatile components.

The other Freons listed in Table 2 should be evaluated as potential surrogates for less volatile and even solid hazardous wastes. The physical state of the surrogate compound should be the same as the POHC under evaluation; e.g. Freon 11 and Freon 113 should be used for volatile POHC's and Freon 22B1 should be used for solid waste. Evaluation of these compounds and further testing of the Freon compounds will be conducted in EPA's pilot scale and laboratory research program to further document the reliability of this technique.

A DIFFERENT APPROACH

The use of Freons and other halogenated organics, used as spiked material in hazardous wastes, may solve many of the problems associated with conducting trial burns. Further improvements, such as a reduction in complexity of analysis requirements, test time, and the associated costs, would be benefits to both industry and government.

An approach which could conceivably accomplish the objectives of shorter test

time and lower cost is to use an altogether different compound such as sulfur hexafluoride (SF₆) [12,18]. SF₆ is a gas which has been widely employed as a tracer in experiments studying atmospheric transport of pollutants [16], meteorology [13], and atmospheric chemistry [5, 7, 8, 10]. Its high thermal and chemical stability, which made it very useful in the above mentioned studies, make it attractive as a potential surrogate for use in hazardous waste incineration trial burns [12, 18]. In addition to these properties, it is non-toxic [9, 14] and is commercially available at relatively low cost [16].

Being a gas, SF₆ cannot be easily or accurately added as a "spike" to liquid or solid hazardous waste. It is most easily introduced into an incinerator or other device by adding it continuously to the combustion air. A potential drawback to this approach is that it may not "simulate" the combustion dynamics, matrix effects or waste form that a POHC experiences. However, it is only a presumption and a theoretical assumption that this method of addition may not be preferred [12]. The practicality and relative low cost of using SF₆ may override any consensus about its suitability as a surrogate.

As part of continuing evaluation of surrogates, the California Air Resources Board and the USEPA sponsored three tests where the feasibility of using SF₆ as a surrogate was investigated. The tests were conducted at a circulating bed combustor (CBC) [4], a dry-process cement kiln and an asphalt plant Table 4 lists the SF₆ destruction and removal efficiencies (DRE) from each test, and the temperature for each process. DRE's for the POHC's in these tests are not yet available. Further studies, specifically devoted to developing the relationship between POHC and SF₆ destruction, are needed before final conclusions can be

Table 3
Freon 113 Feasibility Test Results

<u>Process</u>	<u>Freon 113 DRE</u>	<u>POHC DRE</u>	<u>Process Temperature, °C</u>
Cement	>99.999	>99.996	1500
Aggregate	>99.9999	99.99992	1150
Montmorillonite	>99.99	--	650

Table 4
SF₆ Feasibility Test Results

<u>Facility</u>	<u>DRE</u>	<u>Process Temp °C</u>
Cement Kiln	>99.999%	1500
CBC*	90 - 99.99%	790 - 850
Asphalt Plant	99.3 - 99.8%	190

*Circulating Bed Combustor

drawn on the suitability of SF₆ as a surrogate.

The SF₆ destruction efficiency in the circulating bed combustor varied considerably and appeared to be a function of temperature. In the cement kiln test however, destruction was so complete that SF₆ could not be detected in the stack gas from the kiln. The destruction efficiency was calculated based on the detection limit of the GC/ECD used for the analysis. Freon 113 was also used as a surrogate for this test and its DRE was >99.99%.

The asphalt plant test was quite different from the other tests in that the SF₆ DRE was not very high and the values were confined to a very narrow range.

The significance of these results is that for a range of process temperatures, there is a range of SF₆ DRE. As these were feasibility tests for the evaluation of the concept, further work is needed to establish the relationship between hazardous waste and POHC destruction with SF₆ DRE.

A driving force which might spur further research is the ease with which SF₆ data was collected. By the third test, at the asphalt plant, the experimental protocol had been developed to the point where all of the necessary data could be collected in 4 hours of testing. More than 15 stack samples per hour were taken and analyzed on a semi-continuous basis.

Recently, analyzers developed for continuously monitoring SF₆ concentrations in air, have been used for atmospheric studies [3, 6, 15] and could potentially be adapted for use in stack gas analysis. This would enable a facility operator to have a continuous readout of SF₆ destruction and removal

efficiency. Continuous monitors for SF₆ could also be used to monitor permit compliance on a real-time basis, a tool which environmental agencies do not yet have.

CONCLUSIONS AND RECOMMENDATIONS

Based on feasibility and proof of concept tests, certain Freon compounds and sulfur hexafluoride may prove to be useful surrogates for hazardous waste incineration and be used for permit compliance monitoring. Experiments showed that these compounds are easily introduced into the incineration systems, require relatively simple and low cost equipment such as GC/ECD and are amenable to on-site analysis.

Further work on developing and demonstrating the relationships between surrogate DRE and hazardous waste destruction is recommended. Laboratory and pilot plant research is needed to further develop sampling and analysis protocols, and to make direct comparisons of POHC DRE's with those of surrogates.

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

EVALUATION OF ON-SITE INCINERATION
FOR CLEANUP OF DIOXIN-CONTAMINATED MATERIALS

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ABSTRACT

The EPA Mobile Incineration System (MIS), a kiln-plus-secondary-combustion-chamber-type system, had previously (1982-1983) been tested using PCB-contaminated liquids, and destruction and removal efficiencies of 99.9999% were achieved. Based upon this performance data, a project was initiated to evaluate the technical, economic and administrative viability of on-site incineration for the cleanup of dioxin-contaminated materials. During 1984, the MIS was extensively modified to prepare for field use on dioxin-contaminated soils, and these modifications were tested at Edison, NJ. Additionally, permit documentation, operating and safety protocols, site modification planning documentation, and a risk assessment for the planned trial burn operating conditions were prepared. An aggressive public information activity was conducted by EPA's Region VII office to provide an interested public with planning and permit-related information on the project.

Simultaneously, laboratory and pilot plant studies were carried out to establish optimum kiln conditions for decontaminating soils. These studies indicated that conditions necessary to decontaminate soils thermally could be achieved in the kiln of the MIS. Previous laboratory efforts by others have established that dioxins could be destroyed using time and temperature conditions achievable in the secondary combustion chamber of the EPA system. Therefore, the MIS was judged to have adequate operating conditions for feeding dioxin-contaminated solids and liquids into the kiln, and would have a reasonable chance of success during a dioxin trial burn. The MIS was transported to the Denney Farm site in McDowell, MO, in December 1984.

During 1985, extensive field shakedown activities were conducted during January-March, and a trial burn on dioxin-contaminated liquids and solids was conducted in April. Results from that trial burn indicate that destruction and removal efficiencies exceeding 99.9999% were achieved for 2,3,7,8 TCDD. Additionally, the kiln ash and process wastewater byproducts have been shown to meet "delisting" guidelines proposed by EPA's Office of Solid Waste.

A 30-day field demonstration and a further trial burn on RCRA- and TSCA-designated materials were conducted during the Summer of 1985. These results will also be presented.

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HAZARDOUS WASTE INCINERATION IN INDUSTRIAL PROCESSES: CEMENT AND LIME KILNS

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ABSTRACT

With more liquid wastes due to be banned from land disposal facilities, expanding hazardous waste incineration capacity becomes increasingly important. At the same time, industrial plants are increasingly seeking to find new sources of lower cost fuel, specifically from the disposal of hazardous wastes with heating value.

The Hazardous Waste Engineering Research Laboratory (HWERL) is currently evaluating the disposal of hazardous wastes in a wide range of industrial processes. The effort includes sampling stack emissions at cement, lime and aggregate plants, asphalt plants and blast furnaces, which use waste as a supplemental fuel. This research program is an essential part of EPA's determination of the overall environmental impact of various disposal options available to industry. This paper summarizes the results of the HWERL program of monitoring emissions from cement and lime kilns burning hazardous wastes as fuel.

INTRODUCTION

With the passage of the Hazardous and Solid Waste Disposal Act of 1984, more categories of liquid hazardous wastes will be banned from land disposal facilities. At the same time, energy intensive industries are increasingly seeking to find new sources of less expensive fuel. Because many industrial waste products can be readily used as fuels and some hazardous wastes can be economically processed and made into fuels, a market based on hazardous wastes

has been developing in the U.S. [8], [22]. If reprocessed waste liquids do not contain significant quantities of toxic metals, halogenated materials, and PCBs, and have a high heating value, they can be economically substituted for coal, coke, oil or natural gas in many industrial processes. There are many examples of high temperature industrial furnaces and processes which already burn hazardous waste as supplemental fuel: cement kilns (both wet and dry processes), lime and dolomite kilns, clay processing kilns, steel blast furnaces, phosphate rock calciners and dryers, iron

ore dryers, brick and tile tunnel kilns, mineral wool furnaces and glass melt furnaces.

In particular, there has been a great deal of interest in the use of cement kilns for the disposal of industrial wastes as supplemental fuel for several reasons: 1) the production process is highly energy intensive; fuel savings may translate into a competitive advantage; 2) kiln temperatures are higher (2700°F) and gas residence times are longer (6-10 seconds) than those encountered in most hazardous waste incinerators; 3) cement product quality is relatively insensitive to addition of most waste trace impurities.

The Alternative Technologies Division

of EPA's Hazardous Waste Engineering Research Laboratory-Cincinnati has been investigating hazardous waste incineration in cement kilns since 1977. A number of test programs on waste incineration by other organizations at cement plants have been conducted since 1974 in Canada, the U.S., and Western Europe and are listed in Table I.

The purpose of the tests, both in the U.S. and abroad, was to determine the effectiveness of the process in destroying hazardous wastes, while providing significant heat input into the process. The primary objectives of the test program were to document the performance of each facility and compare it to performance standards promulgated for incinerators. Secondary objectives were to document any

TABLE I. SUMMARY OF CEMENT AND LIME KILN TESTS

Plant	Date	Process	APCD	Fuel	Wastes
1. St. Lawrence Cement Mississauga, ON [3, 12]	1974 1975-76	Dry Wet	ESP ESP	Fuel oil Fuel oil	Waste oil Chlorinated organics
2. Stora Vika Sweden [1, 2]	1978	Wet	ESP	Coal	Chlorinated organics, PCB's, Freon 113
3. Marquette Cement Oglesby, IL [9]	1981	Dry	ESP	Coal	Hydrocarbon solvents ($<5\%$ chlorine)
4. San Juan Cement Puerto Rico [17]	1981-82	Dry	ESP	Coal	Chlorinated organics
5. Alpha Cement Cementon, NY [15]	1982	Wet	ESP	Coal	Solvents
6. General Portland Lebec, CA [10]	1982	Dry	Baghouse	Coal	Hydrocarbon solvents
7. General Portland Paulding, OH [4]	1983	Wet	ESP	Coal	Hydrocarbon solvents Freon 113
8. Lone Star Industries Oglesby, IL [5]	1983	Dry	ESP	Coal/Coke	Hydrocarbon solvents Freon 113
9. Rockwell Lime Manitowoc, WI [7]	1983	Lime	Baghouse	Coke	Hydrocarbon solvents

changes in conventional pollutant emissions that could be attributed to burning hazardous waste and identify new problems.

This paper summarizes the data from these tests on: waste destruction and removal efficiency (DRE), hydrogen chloride (HCl) emissions, and changes in conventional pollutant emissions from kilns when burning hazardous wastes as supplemental fuel. From the RCRA standpoint, most important of these concerns are particulate matter, (DRE), and HCl results. Carbon monoxide, NO_x , total hydrocarbons (THC), and SO_x will also be discussed. For reference, a generalized diagram of a cement kiln burning waste as a fuel is shown in Figure 1.

PARTICULATE MATTER

Most of the tests conducted at kilns using electrostatic precipitators exhibited small or little change in particulate emissions when burning hazardous wastes. A summary of the average data for each test is listed in Table II. The major exceptions are tests during which there were either process equipment malfunctions [5, 12] or high amounts of chlorine being fed to the kiln (1, 2, 12). The latter tests have led to the conclusion that the higher chlorine input to the kiln will lead to greater particulate emissions.

In a review article, Weitzman [21] discussed particulate emissions from cement kilns burning chlorinated wastes as fuel. Data from the St. Lawrence Cement and Stora Vika tests were re-examined, compared, and were plotted as a function of chlorine feed rate. The resulting graph showed a linear increase in particulate emissions as a function of chlorine input to the process. In the article, he hypothesized that the hydrogen chloride combustion product reacts with the potassium, sodium, and calcium compounds in the hot kiln to form the respective chlorides and the volatilized chloride salts were carried by the hot gas to the cooler end of the kiln where they condensed at about 800°C to form a fine particulate. The higher chloride content of the particulate, with concomitant changes in dust resistivity, lowered the electrostatic precipitator (ESP)

collection efficiency. This resulted in significantly increased dust emissions during the two chlorinated organic waste firing tests. Based on the results of these tests and the hypothesis of very fine particles, Weitzman concluded that a kiln using a fabric filter for particulate removal would encounter a similar deterioration in efficiency.

The particulate emissions from the kiln tested at San Juan Cement [17], equipped with a fabric filter dust collecting system, did not exhibit an increase with progressively larger chlorine input as shown in Figure 2. For comparison, the linear regression plot developed from the St. Lawrence Cement and Stora Vika data are also displayed. It can be seen that, not only was more organic chlorine fed to the kiln at San Juan Cement than more of the previous tests, the fabric filter system was able to maintain a high collection efficiency regardless of the amount of chlorine fed to the kiln.

Thus, the addition of substantial amounts of organic chlorine in waste fuel may contribute to lowering ESP collection efficiency, but has no effect on control efficiency of fabric filters. [14]

DESTRUCTION AND REMOVAL EFFICIENCIES FOR PRINCIPAL ORGANIC HAZARDOUS CONSTITUENTS

Incinerators and, in the near future, other facilities burning hazardous wastes, must perform at a minimum to the standards described in the Federal regulations [20]. Specifically, with regard to the Principal Organic Hazardous Constituents (POHC's), the facility must achieve a destruction and removal efficiency (DRE) of 99.99% for each designated POHC. The DRE is determined as follows [20]:

$$\text{DRE} = \frac{W_{\text{in}} - W_{\text{out}}}{W_{\text{in}}} \times 100\%$$

where: W_{in} = mass feed rate of a specific POHC in waste feed stream.

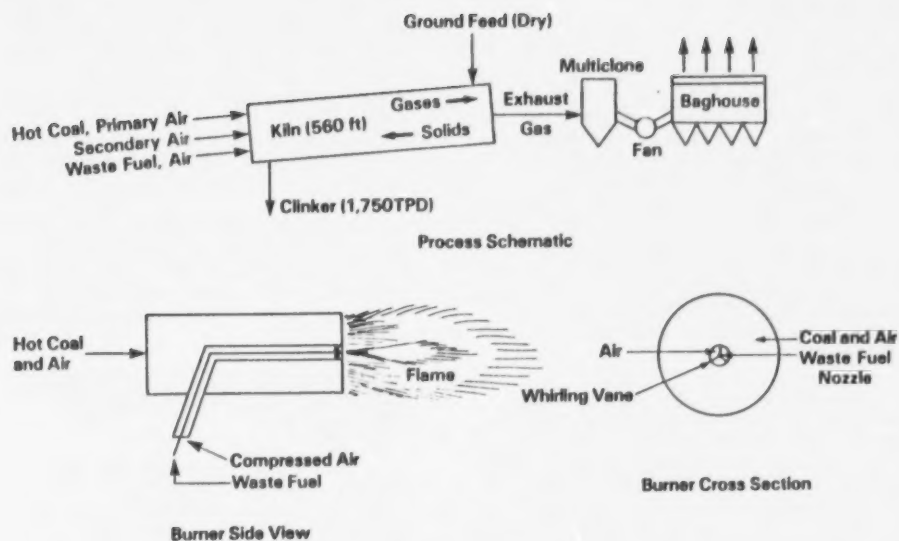


Figure 1. Generalized Diagram of a Cement Kiln Burning Hazardous Waste

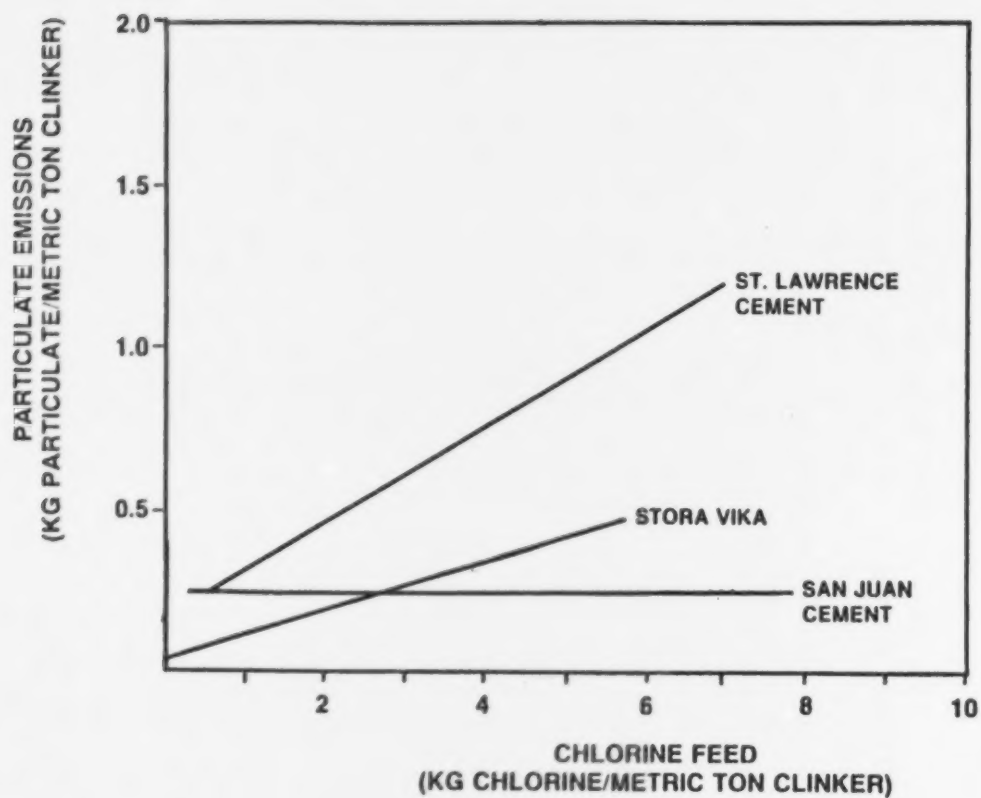


FIGURE 2. Illustration of the Variation of Particulate Emissions with Chlorine Feed

TABLE II. SUMMARY OF PARTICULATE EMISSION DATA

Plant	Test Condition	Particulate Emissions			Chloride Input to Kiln (kg/Mg)
		gr/scf	lb/hr	lb/ton	
St. Lawrence	Chlorinated aliphatics ¹	0.21	123	3	4.0
	Chlorinated aromatics	0.286	45	1.1	5.5
	PCB's	0.078	44	1.1	2.5
	Baseline	0.038	21	0.5	-
Rockwell Lime	Lubricating oil	0.064	83	0.7	-
	Baseline	0.107	139	1.1	-
	Waste	0.016	2.2	0.26	2.7
	Baseline	0.013	2.0	0.24	-
Stora Vika	Aliphatics	0.039	21	0.88	4.4
	Baseline	0.009	4.7	0.21	0
	PCB's	0.024	12.7	0.53	3.6
	Baseline	0.011	5.9	0.25	0
Marquette	Chlorophenols	0.058	30.9	1.36	0.95
	and Phenoxyacids				
	Baseline	0.014	7.7	0.34	0
	Freon 113	0.062	33.3	1.39	1.7
Alpha Cement	Baseline	0.022	11.7	0.49	0
	Waste solvents	0.014	58	21	1.1
	Baseline	0.093	80	20.8	-
	Solvents	0.041	44	0.8	-
San Juan	Baseline	0.050	53	1.1	-
	Wastes	0.043	22.4	0.66	5.5
	Baseline	0.041	21.7	0.64	-
	Wastes	0.030	18.9	0.65	2.2
General Portland Paulding	Baseline	0.030	19.6	0.64	0.2
	Waste ²				
	Baseline	0.17	116	2.0	1.2
					0.2

¹ Process upset during test² ESP malfunctioned during test

W_{out} = mass flow rate of the same POHC in exhaust emissions to the atmosphere.

Table III summarizes the results of the tests which revealed reliable DRE data.

One of the first tests to examine the DRE of hazardous waste in cement kilns was conducted at a Canadian plant, St. Lawrence Cement. The wet-process kiln was normally fired with fuel oil and the exhaust gas was cleaned by an ESP. Three tests were conducted with batches of waste solvents labeled as chlorinated aliphatics, chlorinated aromatics, and PCBs. The chlorinated aliphatics were composed primarily of chloropropane, chloropropene, 1,2-dichloroethane, 1,1,2-trichloroethane, and chlorobenzene. The chlorinated aromatics batch was primarily chlorotoluene, and the waste labeled PCBs was about 50 percent PCB, 28.5 percent chlorotoluene, and a mixture of chlorinated aliphatics. Destruction efficiencies were calculated conservatively by not subtracting or correcting for the background levels from the baseline test or interferences (contamination) on the control blanks. In addition, a conservative collection efficiency of 80 percent was used. The result was a maximum estimated concentration of 50 ppb for all of the waste fuel tests, and "because of the high and uncertain background levels, the estimate of emissions is higher than the actual levels in the emissions" [12]. The DREs were calculated on total chlorinated organics basis rather than on the actual analysis of specific compounds. The reported DREs for wastes with mostly chlorinated organics was >99.99 percent, >99.989 percent for chlorinated aromatics, and >99.986 percent for PCB mixtures [12].

A test similar to the one conducted at St. Lawrence was conducted in Sweden at a wet process kiln in Stora Vika. Short-term tests were conducted with chlorinated aliphatics (100 hr), PCBs (24 hr), chlorophenols and phenoxy acids (12 hr) and trichlorotrifluoroethane (Freon 113) (3 hr). Long-term tests were conducted with the chlorinated organics (1.5 months) and PCBs (about 1 month).

Results are listed in Table III. During both the short- and long-term tests with chlorinated aliphatics, none of the

waste fuel's major components were detected in the stack gas. Based on the detection limit, the DRE of methylene chloride exceeded 99.995 percent and the DRE of trichloroethylene exceeded 99.9998 percent [1], [2].

No PCBs were detected in the stack gas during either the short- or long-term test and yielded a DRE exceeding 99.99998 percent for PCB. Similarly, no chlorophenols or phenoxy acids were detected in the stack gas; DREs were calculated to be greater than 99.99999 and 99.99998 percent, respectively. Detectable levels of Freon 113 were found during one experiment with this waste fuel and yielded a DRE of 99.99986 percent [1], [2].

The test at the General Portland's Los Robles dry process kiln included dichloromethane, 1,1,1-trichloroethane, 1,3,5-trimethylbenzene, and xylene as POHC's in the waste fuel. The results show a DRE of 99.99 percent or greater for 3 of the 4 compounds and again, the calculations are conservative. No corrections were made for baseline levels or for the contribution from ambient air. No trimethylbenzene was detected; therefore, the DRE for this compound is likely to have exceeded 99.95 percent [10].

In the tests at General Portland's Paulding, Ohio plant, DRE's for the most part were greater than 99.99 percent and in some cases higher than 99.999 percent. DRE's less than 99.99 percent for methyl ethyl ketone and methylene chloride were related to sample contamination problems and do not represent poor incineration performance of the kiln. No problems with contaminants were seen with the 1,1,1-trichloroethane and Freon 113 results, which demonstrated DRE's of 99.999 percent or greater.

The results of the test burn at Lone Star showed similar contamination problems with methylene chloride. However, the DRE's for other compounds were all greater than 99.99 percent on conservative basis; i.e., no correction for blanks. In addition to the POHC's, several other compounds were tracked for DRE. Styrene, ethyl benzene, orthoxylene, and benzaldehyde all showed DRE's greater than 99.998%, which indicates that excellent destruction conditions existed in the kiln [14].

TABLE III. SUMMARY OF DRE DATA

Plant	Waste Component	Destruction Efficiency
St. Lawrence Cement	Chlorinated aliphatics	>99.990
	Chlorinated aromatics	>99.989
	PCB's	>99.986
Stora Vika	Methylene chloride	>99.995
	Trichloroethylene	>99.9998
	All chlorinated hydrocarbons	>99.988
	PCB	>99.99998
	Chlorinated phenols	>99.99999
	Phenoxy acids	>99.99998
	Freon 113	>99.99986
San Juan Cement	Methylene chloride	93.292-99.997
	Carbon tetrachloride	91.043-99.996
Los Robles (General Portland)	Methylene chloride	>99.99
	1,1,1-Trichloroethane	99.99
	1,3,5-Trimethylbenzene	>99.95
	Xylene	>99.99
Paulding (General Portland)	Methylene chloride	99.956-99.998
	Freon 113	>99.999
	Methyl ethyl ketone	99.978-99.997
	1,1,1-Trichloroethane	99.991-99.999
	Toluene	99.940-99.988
Oglesby (Lone Star)	Methylene chloride	99.94-99.99
	Freon 113	99.999
	Methyl ethyl ketone	99.997-99.999
	1,1,1-Trichloroethane	>99.999
	Toluene	99.986-99.998
Rockwell Lime	Methylene chloride	99.9947-99.9995
	Methyl ethyl ketone	99.9992-99.9997
	1,1,1-Trichloroethane	99.9955-99.9982
	Trichloroethylene	99.997-99.9999
	Tetrachloroethylene	99.997-99.9999
	Toluene	99.995-99.998

Waste fuel containing methylene chloride, methyl ethyl ketone, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and toluene was burned during the test at Rockwell Lime. The average DRE results are listed in Table III and show an average of 99.99 percent or greater. The reported DREs are again conservative because no blank corrections were applied. DREs exceeding 99.99 percent were consistently obtained for all POHCs.

The test at San Juan used methylene chloride, chloroform, and carbon tetrachloride as the designated POHCs in a waste fuel with very high chlorine contents (6.5-35.1 percent). This test showed a phenomenon seen at other cement kiln tests: measurable emission rates of the POHCs during the baseline test when no waste was burned. Blank samples showed no contamination problems; therefore, the source of the POHCs during the baseline was unexplainable. The reported DREs for this test (Table III) are low compared with other test results. The test report concluded that lack of air atomization of the waste fuel and the difficulty of incinerating highly chlorinated monocarbon compounds contributed to the low DREs. Above normal free lime content of the clinker product and removal of chloride in the clinker instead of the waste dust also suggest that operating difficulties were experienced in the kiln. However, the detection of POHCs during the baseline make the DRE results difficult to interpret. If the measured POHCs originated from sources other than burning waste fuel, the actual DREs may have been higher than those measured [17].

The San Juan test, when viewed with results from other cement kiln tests, suggests that burner design, waste composition, and the kiln's operation can have a significant effect on DRE performance. The extent of their effect is inconclusive because of baseline POHC emissions.

CARBON MONOXIDE AND TOTAL HYDROCARBONS

CO emissions are not affected by the burning of waste fuels. Weitzman noted that changes in CO can be indicative of flame quenching, improper burner adjustment, or other imbalances in the flame [21]. Peters and Mournighan [14] found that any process change can create a significant

CO excursion. Examples of process changes include alteration of: the primary air/fuel ratio, secondary air flow, solid fuel feed rates, and product cooler exhaust flow. These effects were observed during the Paulding test during a kiln upset with coal as the only fuel. Over the course of the event, several process parameters were changed and large swings in CO concentrations (as well as other monitored gas concentrations) were observed. The CO results for Stora Vika also show a wide range of 50-1500 ppm for both the baseline and waste fuel burns. Table IV lists CO and total hydrocarbons for each of the tests.

The CO results for Lone Star appear to be the most consistently low. The kiln was operated with a higher O₂ input (to aid in drying wet coal), which apparently resulted in consistently low levels of THC, CO and SO₂ with increased NO_x concentrations. The Los Robles kiln was also very stable during three waste firing tests in which the maximum CO was 100 ppm.

The CO results indicate that the feeding of waste fuel to the kiln does not significantly affect CO concentrations. Process stability apparently has a greater effect on CO concentrations. CO monitors on kilns provide the operator with a measure of this stability. The CO measuring equipment in general use by the industry is not as sensitive as the equipment used by the test crews and is not capable of seeing CO concentrations much below 1000 ppm. Installation of more sensitive CO monitors would help operators control combustion conditions more effectively.

Total hydrocarbons (THC) increased during waste fuel combustion at 3 tests, decreased at 2 tests, and remained the same at another. The consistently low THC concentrations for several different types of compounds at Stora Vika suggest that kiln operation may affect THC concentrations more than the waste type does. The levels at Rockwell Lime, which attained consistently high DRE's, averaged 3.5 ppm. Similarly, the Lone Star kiln maintained consistently low levels of THC between 2.5 and 5 ppm. These data for different types of kilns and wastes fuels indicate that a well-controlled kiln can operate with average THC concentrations below 10 ppm.

TABLE IV. SUMMARY OF THE THC AND CO CONCENTRATIONS

Site	Test condition	THC (ppm) _a	CO (ppm)
San Juan	Waste burn	12.7	24 - 738 ^b
	Baseline	8.3	25 - 349 ^b
Los Robles	Waste burn	^c	25 - 100
General Portland	Baseline	4	10 - 618
Paulding	Waste burn	21	190
General Portland	Baseline	10	212
Lone Star	Waste burn	5	24 - 49 ^b
	Baseline	2.5	35 - 40 ^b
Rockwell Lime	Waste burn	3.5	599
	Baseline	8.2	477
Stora Vika	Chlorinated aliphatics	<10	300 - 1500
	Baseline	<10	1,500
	PCBs	<10	100 - 1500
	Baseline	<10	100
	Chlorophenols/phenoxy acids	10	50 - 500
	Baseline	10	50
	Freon	<10	100 - 500
	Baseline	<10	100

^a Expressed as ppm methane unless otherwise noted.

^b Range of test averages.

^c Not measured.

NITROGEN OXIDES

In cement and lime kilns, there is a direct functional relationship between NO_x emissions and secondary combustion air flow and temperature. There is usually little or no NO_x formed from nitrogen in fuel relative to NO_x from combustion air. Kilns are generally operated as "poor" combustors. When compared to boilers and incinerators, kilns have a reduced primary air/fuel mix, poorer secondary air mixing, and often require a confined, narrow flame configuration for good product quality. Typical NO_x concentrations in the stack gas can range from 200 to 1500 ppm, depending on combustion conditions. NO_x levels are very operator-dependent; continuous monitoring has shown that at some kilns NO_x levels vary widely from hour to hour, while others can maintain steady NO_x concentrations for days at a time. These and other tests conducted under the USEPA NO_x Reduction Program [18] indicate that waste firing has little to do with NO_x variations. The amount of excess air, secondary air temperature, and primary air/fuel ratios are the main determinants in kiln NO_x emissions [14].

Table V present a summary of the tests for which NO_x emissions data is available. At both Marquette Cement and San Juan Cement a significant decrease was observed during waste firing. This may have been the result of lowered oxygen input more than waste firing. At the General Portland - Los Robles Plant, the NO_x emissions decreased slightly the change was not statistically significant. A significant increase was observed at Rockwell Lime, but the change was intended so that the NO_x emissions increased during waste firing.

A definite relationship between O_2 , NO_x , and SO_2 in calcination kilns has been shown [18]. NO_x emissions decrease with decreasing O_2 input and lower secondary air temperatures, while SO_2 emissions increase. For instance, a 38% reduction in NO_x due to O_2 lowering can cause a 47% increase in SO_2 . Continuous monitoring at Rockwell Lime and General Portland-Paulding illustrated that NO_x and SO_2 change inversely, as shown in Figure 3. Moreover, the NO_x/SO_2 change is followed within 5-15 minutes by a CO spike, the kiln's indicator of a momentary process instability. As shown in Figure 3, this event recurred at uneven intervals.

ACID GASES

The process materials in cement kilns, by their alkaline nature, provide built-in control for acid gases such as SO_2 and HCl . In a well operated cement kiln with medium-to high feed alkalinity, SO_2 will be scrubbed in the kiln environment and be adsorbed by the alkaline dust of the air pollution control device to control efficiencies of greater than 90%. For HCl emissions, a removal of efficiency greater than 99% was observed at San Juan Cement, where high amounts of chlorine were added to a kiln processing relatively low alkaline materials [17]. Tables VI and VII present the emission results for SO_2 and HCl , respectively, for all tests.

As shown in Table VII, HCl results are quite variable from test to test. For the most part, however, HCl emissions are low and less than the standard set for incinerators [19]. Notable exceptions are the Marquette and Lone Star tests. The results of the Lone Star tests are suspect because of ESP malfunction.

Waste fuels typically do not contain much sulfur and thus the partial substitution of waste fuel for fuel oil or coal will reduce sulfur input to the kiln, resulting in less SO_2 to being formed. During the Marquette Cement test, where a 13% energy substitution was fired, SO_2 stack gas concentrations were reduced from 93 ppm to 18 ppm. At the Los Robles cement plant, no significant difference in SO_2 emissions was noted. SO_2 emissions increased significantly at San Juan Cement, from 280 ppm to 450 ppm, probably for two reasons: the NO_x emissions were reduced--indicative of lower O_2 input--and the high rate of chlorine input may have caused a competitive acid gas "scrubbing" situation-- HCl was preferentially absorbed over SO_2 . The kiln operator's choice of O_2 input will have a greater effect on SO_2 emissions than addition of a waste fuel. The test results indicate that it is possible, and probably preferable to operate a cement kiln with less than 50 ppm SO_2 in the stack gas, when burning hazardous waste.

At Rockwell Lime, however, a different mode of operation was required; SO_2 is not intentionally absorbed because the presence of sulfur in their lime product is undesirable. No significant difference was observed for SO_2 emissions, which

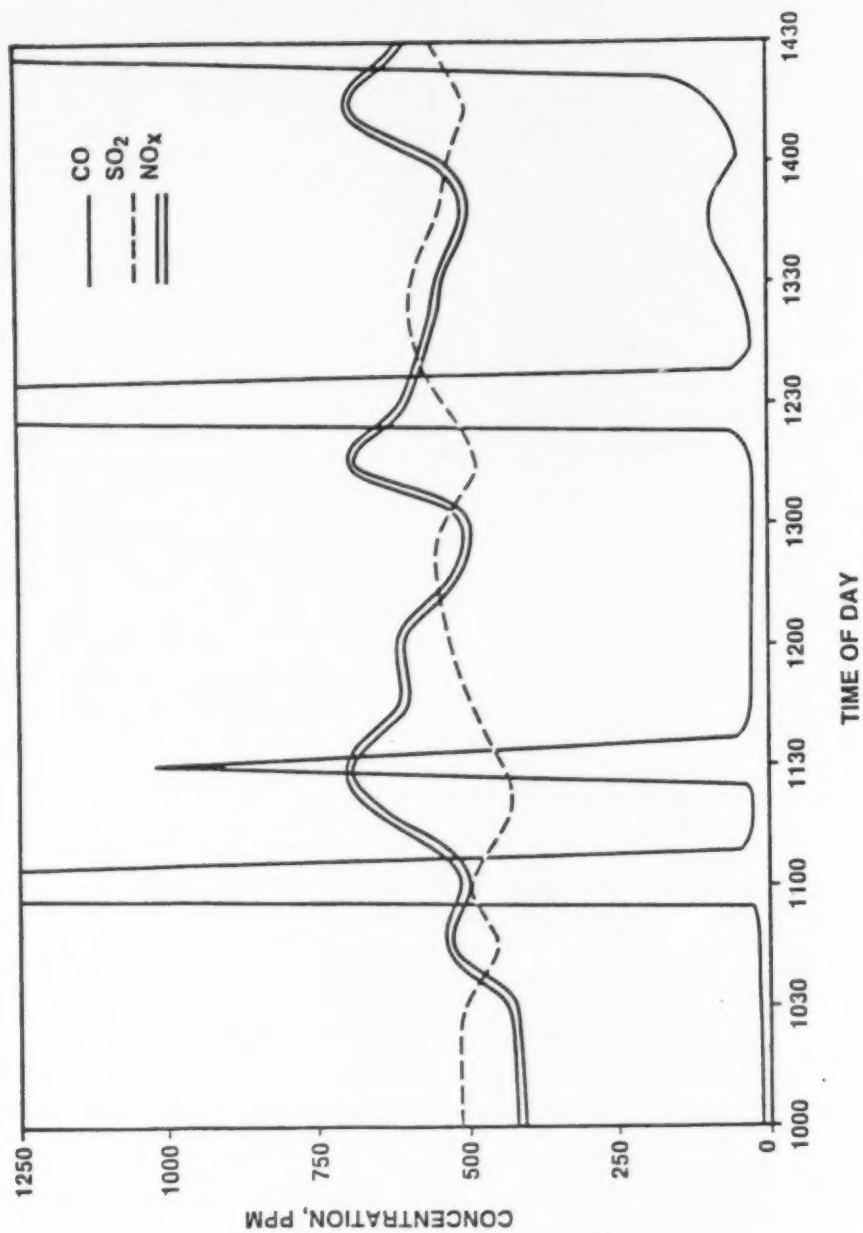


Figure 3. Illustration of Interrelationship Between NO_x, SO₂, and CO Emissions in a Lime Kiln

TABLE V. SUMMARY OF NO_x EMISSIONS DATA

Test	Condition	(lb/hr)	NO _x (lb/ton)	(ppm)	Comments
Marquette	Waste Baseline	275 404	4.6 6.7	544 920	Significant decrease in NO _x
San Juan	Waste Baseline	31.3 60.4	0.9 1.8	68 136	Significant decrease in NO _x
Los Robles	Waste Baseline	304 444	5.3 8.2	486 680	No significant decrease in NO _x
Paulding	Waste Baseline	174 140	6.0 4.6	478 371	Significant increase in NO _x
Lone Star	Waste Baseline	472 371	8.6 6.9	814 620	Significant increase in NO _x
Rockwell Lime	Waste Baseline	- 134	- 15.8	446 386	Significant increase in NO _x

remained between 500-600 ppm regardless of waste firing.

The data indicate that effects of chlorinated waste combustion on HCl emissions are quite variable from kiln to kiln. Variations in HCl emissions with time can also exist within the same kiln, depending on operating conditions. Sporadic variations in HCl can be expected because of cyclic temperature variations, feed and fuel changes that affect the kiln temperature profile, and chloride loading, and variations in recycle dust rate and composition.

The continuous monitoring of SO_2 , NO_x , O_2 and CO indicated that the concentration of these compounds in the stack gas are interdependent and combustion operation can be optimized. Use of continuous monitors proved to be an excellent process monitoring tool because of the increased information feedback on combustion conditions. Although continuous monitoring equipment requires constant attention and maintenance, their worth as a process control tool may prove quite valuable.

CONCLUSIONS

The foregoing examples of burning liquid hazardous wastes as a fuel supplement in cement and lime kilns in Canada, Sweden, Illinois, Puerto Rico, California, and Wisconsin have demonstrated that there is little or no significant change in emissions of conventional pollutants and that process operation changes have a greater effect on changes in emissions than the partial substitution of hazardous waste fuel.

The conventional pollutants which show little or no significant change and are independent of hazardous-waste-as-fuel burning are CO, THC, NO_x and SO_2 . Previous studies and evaluation of continuous monitoring demonstrated that emission rates of these compounds are more a function of combustion air flows and fuel rate control than any of the other parameters.

Particulate emissions from kilns equipped with electrostatic precipitators may be expected to increase with increasing chlorine loading in the kiln. Those kilns equipped with fabric filters, or baghouses, will not experience any significant change in emissions.

HCl emissions from cement and lime kilns meet emission limits set for incinerators. However, variations in test results warrant further investigation into this issue.

Destruction and Removal Efficiencies (DRE) of POHC's were, for the most part, greater than the incinerator regulatory requirement of 99.99%. It appears that there are enough variations in kiln operation from plant to plant, that variations in DRE would be expected, but a well operated facility should have little trouble in demonstrating compliance with the DRE requirement.

TABLE VI. SUMMARY OF SO₂ EMISSION DATA

Test	Condition	(lb/hr)	SO ₂ Emissions (lb/ton)	(ppm)	Comments
Alpha Cement [19]	Waste Baseline	58.5 138	1.1 2.7	33 78	S in coal = 2.6%; S in waste = 0.2% S during waste burn = 2.0%
Marquette	Waste Baseline	11.5 57.1	0.19 0.95	18 93	S in waste = 0.08% Significant decrease
San Juan	Waste Baseline	264 170	8 5	450 279	S in fuel oil = 2.15% Significant increase
Los Robles General Portland	Waste Baseline	21.7 23.7	0.36 0.38	27 27	S in coal = 0.43% No significant difference
Paulding General Portland	Waste Baseline	297 526	6.8 17.2	265 635	S in coal = 4.3% Significant decrease
Lone Star	Waste Baseline	6.7 5.6	.12 .10	19 7	S in coal/coke = 2.7% Significant increase
Rockwell Lime	Waste Baseline	97 149	11.4 17.5	596 553	S in coke = 4.15% No significant difference

TABLE VII. SUMMARY OF HCl EMISSION DATA

Test	Condition	HCl Emissions	
		(lb/hr)	(lb/ton)
Alpha Cement	Waste	5.8	0.11
	Baseline	2.4	0.05
Marquette	Waste	115	1.9
	Baseline	190	3.2
San Juan	Waste	0.79	0.02
	Baseline	0.19	0.006
Los Robles (General Portland)	Waste	1.03	0.015
	Baseline	0.55	0.007
Paulding (General Portland)	Waste	4.62	0.16
	Baseline	1.25	0.04
Lone Star	Waste	25.3	0.46
	Baseline	2.9	0.054
St. Lawrence	Waste	1	0.02
	Baseline	1	0.02
Rockwell Lime	Waste	0.44	0.05
	Baseline	0.20	0.02

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Disclaimer

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer and administrative review policies and approved for presentation and publication.

COMBUSTION FUNDAMENTAL STUDIES FOR HAZARDOUS WASTE INCINERATION

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ABSTRACT

This paper discusses Union Carbide's fundamental research program being conducted to better understand the spray combustion of liquid chemical wastes. The program focuses on the study of turbulent mixing phenomena in the flame zone and constitutes a fuel atomization study and a 3-million Btu/hour research combustor swirl combustion study. The installation and initial start-up troubleshooting were completed for both facilities in December, 1984. The actual test program is on-going.

INTRODUCTION

In the past, the design and operation of a chemical waste incinerator was mostly an art and not a science. The performance of an incinerator was basically determined by visual observation of the flame pattern and color. Trial and error, and each individual company's past experience were the sources of information. Although this approach has been satisfactory, better scientific understanding of the design and operating principles is needed in order to be sure that the stringent regulatory requirements for the combustion of hazardous waste can be met.

From our many years experience in operating various chemical waste incinerators, we have learned that the performance of an incinerator is determined basically by the

design and the operation of the system and not by kinetics. Incineration can be a very reliable operation if the system is designed and operated properly. This observation is also supported by several trial burn test related programs (4, 13) conducted in the past few years. Those tests also found that the incinerability of each individual organic compound is really not an important factor to be considered in evaluating the performance of an incinerator under flame conditions. If an incinerator is designed and operated with the capability to destroy one compound, which is reasonably stable (thermally), the chances are that it can destroy other compounds. If one compound fails to meet a 99.99% destruction and removal (DRE) for a good incinerator, the chances are that either the

compound is a combustion intermediate of other compound(s), or the compound has a very low concentration (between 100 to 1000 ppm) in the waste feed.

Union Carbide has contributed to the advancement of knowledge in flameless thermal oxidation (11). However, in the real world, the factors which really impact on organic destruction in a liquid injection incinerator are those things which happen in the flame zone and not what happens in the post-flame zone.

In view of this, Union Carbide has constructed a fuel (waste) atomization facility and a research combustor facility to advance the knowledge of liquid injection chemical waste combustion.

PURPOSE

In a liquid waste incinerator, waste is normally atomized into a mist. The organics have to be vaporized before they can be burned. The waste mist is mixed with combustion air in the burner zone. As will be shown later, the most critical factor affecting the destruction efficiency of liquid wastes often is the performance of the burner nozzle. The pattern of turbulent mixing of the combustion air with the mist is also critical; the right amount of oxygen has to be supplied to the burning mist droplets at the right time and right location. For a well-designed and properly-operated incinerator, most of the organic destruction occurs near the flame zone

through flame oxidation processes. What takes place in the combustion chamber after the flame zone is relatively less critical because the combustion chamber (or what is normally called incineration) temperature is much lower than the flame zone temperature. The gas flow in the rest of the combustion chamber is normally somewhat stratified. The combustion chamber just provides additional time and temperature to destroy the trace organics left over from the flame zone. This occurs through much slower flameless thermal oxidation processes.

If the three T's of combustion for liquid injection waste incinerators are ranked, "Turbulence" is the most important, followed by "Temperature" and "Time". Time is the least important factor of the three if a certain minimum operating temperature (between 1,500 to 1,600°F) is met and good turbulence has been achieved. The temperature and time considerations are related to the reaction kinetics or the chemical processes of the combustion. The turbulence consideration is related to the very complex and difficult to handle physical processes of the combustion. Factors which have impact on the turbulence include: fuel atomization, droplet's size distribution, droplet's evaporation or gasification rate, air/fuel mixing pattern and rate, stages of air addition, etc. Just about any design and operating parameters have impacts on turbulent mixing.

In the past few years, laboratory studies (7, 11) were conducted to study the destruction of organics under non-flame conditions. Results from those studies have indicated that above 1500°F (820°C), the reaction rate is so fast that, theoretically, less than 0.1 second is required to achieve the 99.99% DRE requirement. At temperatures higher than 1600°F (870°C), any organic compound will be destroyed in no measurable time (again, theoretically). We all know that in the real world case, this does not happen due to the fact that the reaction rate is mixing- (or mass transfer-) limited and not kinetics-limited.

Calculated results shown in Table I demonstrate those points discussed. Non-flame kinetics data for vinyl chloride (which is known to be thermally stable) are used in the calculation. The detailed data and equations used can be found in Reference 11.

Of the many physical processes going on in a flame zone, fuel atomization is the most critical step. Many theoretical studies have been conducted on either single droplet combustion phenomena, or the combustion of vapor cloud (6, 8, 10). All those studies tell us that the liquid fuel combustion is very

TABLE I
Theoretical Vinyl Chloride Destruction Efficiency Calculation

(Note: The number shown below is "the fraction remaining" which is one minus the destruction removal efficiency (DRE).)

<u>Residence time</u>	<u>0.1 sec</u>	<u>0.5 sec</u>	<u>1.0 sec</u>
Temperature			
1200°F	9.66 x 10 ⁻¹ (3.4% DRE)	8.4 x 10 ⁻¹ (16.% DRE)	7.0 x 10 ⁻¹ (30.% DRE)
1300°F	7.8 x 10 ⁻¹ (22.% DRE)	2.9 x 10 ⁻¹ (71.% DRE)	8.2 x 10 ⁻² (92.% DRE)
1400°F	2.4 x 10 ⁻¹ (76.% DRE)	7.4 x 10 ⁻⁴ (99.926% DRE)	5.4 x 10 ⁻⁷ (99.999946% DRE)
1500°F	9.5 x 10 ⁻⁴ (99.905% DRE)	7.6 x 10 ⁻¹⁶	5.7 x 10 ⁻³¹
1600°F	3.0 x 10 ⁻¹³	2.4 x 10 ⁻⁶³	1.0 x 10 ⁻⁹⁹
1650°F	5.8 x 10 ⁻²⁵	1.0 x 10 ⁻⁹⁹	1.0 x 10 ⁻⁹⁹

complex. In the near future, no satisfactory theoretical or mathematical solutions can be resolved to fully understand the fuel atomization and the associated combustion phenomena. The addition of the swirl mixing with air makes the problem even more complex. In our opinion, the best way to resolve those problems is a statistically designed experimental program followed with statistical data analyses to obtain some kind of empirical correlations.

Several experimental fuel atomization studies are ongoing (3, 5, 9) to address the importance of spray combustion. This also indicates the lack of fundamental knowledge in this area. Typical fuel oils have to meet certain ASTM standards and have defined fuel properties. This is not the case for chemical wastes. A variety of physical and chemical properties are possible for chemical wastes. Hence, the study of atomization for chemical wastes is even more difficult.

Information on spray nozzle performance alone is of little use without an actual performance evaluation under flame combustion conditions. The smallest, practical spray nozzle for chemical wastes is around three million Btu/hr due to plugging considerations. Hence, we have built a multiple purpose, pilot-scale research combustor to further evaluate the nozzle performance which has been determined to be satisfactory from

the cold-fuel atomization study, under flame conditions.

The majority of the RCRA Appendix VIII compounds are chlorinated chemicals. The others are basically nitrogen- and sulfur-containing chemicals. Hence, one goal of our flame combustion study is to assess the design and operating conditions which favor the destruction of chlorinated compounds. At a later time, we would also like to evaluate the combustion of nitrogen- and sulfur-containing chemicals.

Emission of Products of Incomplete Combustion (PICs) is becoming of concern to the general public. Although the emission of incomplete combustion products is a phenomenon of all combustion devices and the trace level emitted from an incinerator may not present any more threat to public health and environment than the other combustion devices, we would like to understand this problem better with our research combustor.

The objectives of the Union Carbide combustion fundamental research can be summarized as:

- o To develop a better understanding of what is going on in the flame zone when chemical wastes of different chemical and physical properties are burned.

- o To develop design and operating criteria to maximize the organic destruction effi-

ciency and minimize the production of incomplete combustion intermediates.

APPROACH

Two test facilities have been constructed at Union Carbide's South Charleston Technical Center to carry out the fundamental chemical waste combustion studies. One is a cold, non-flame fuel atomization pilot unit and the other is a flame combustion multiple-purpose pilot test unit.

Fuel Atomization Pilot Facility

It is very difficult to conduct atomization tests on hazardous wastes due to the many concerns of safety, health, and environment. The three major considerations in the design of the test facility are: the safe handling of the waste material, the explosive nature of the fuel mist and air mixture, and the recovery of all spray droplets and vapor from the exhaust gas.

A schematic diagram of the fuel atomization pilot facility is shown in Figure 1. The facility can be functionally separated into four parts: (a) fuel handling system; (b) spray vessel; (c) effluent gas organic emission control system; and (d) emergency shutdown system.

The fuel handling system allows the test liquid to be transferred in a closed system

between a fuel feed drum, a spray test vessel, and a waste storage drum. The fuel lines are designed to allow maximum flexibility in operation during the test. The waste liquid (including the line purging solvent) is contained in the waste storage drum after the test. Drum heaters and heating tapes are used to control the test fluid viscosity.

The two-foot diameter spray vessel is designed as a pressure vessel able to contain an explosion. An explosion is very unlikely to occur since all potential ignition sources are eliminated. Every part of the unit is properly grounded to avoid accumulation of static charges. The vessel is equipped with two, 6 x 10-inch viewing windows and two, 6 x 6-inch windows for optical diagnosis. In one of the test setups, a honeycomb metal plate can be inserted above the window to stratify the screening gas to avoid fogging of the windows by the fuel mist. The vessel is operated under slight vacuum to avoid fugitive organic emissions.

An exhaust fan is used to remove the gas and droplet mixture from the test vessel and create a slight negative pressure. The desired pressure level can be adjusted through a damper. Following a droplet knock-out device, a wiremesh filter and a fabric filter are currently used as a two-stage demister to remove

all liquid droplets from the exhaust gas before it is discharged into the atmosphere. This demister has performed satisfactorily in the initial tests.

The safe operation of the test facility is further ensured by an emergency shutdown system. Both the fuel and air influent flows will be shut off automatically in case any one of the following conditions occur:

- o Overheating of the test liquid in the fuel management system.
- o Pressure build-up in the spray vessel.
- o Overfilling of the test liquid in the spray vessel.
- o Loss of the exhaust fan.

Two techniques are currently used for spray diagnosis: visual observation and photography. The visual observation of the spray provides the preliminary operational information of the test waste atomizer. Two still picture camera systems are used to study the sprays. A 35-mm camera system is used for spray structure study and a 4 x 5-in. format camera system is used for in-depth spray quality analysis. A single-flash shadowgraphic technique was used (Figure 2) for picture taking. These camera systems are similar to those used by researchers at Carnegie Mellon University (5).

Multiple-Purpose Research Combustor

The research combustor system consists of several skid-mounted modules. Maximum flexibility was the key idea in the design of the research combustor. The system was designed to be able to test different burners, nozzles, and fuels with different properties. In the initial stage, a research burner developed by the International Flame Research Foundation is being used extensively to study the impact of various air mixing patterns on the flame zone. Other burners will be studied at a later time. The research combustor is designed to have a long residence time (about 4 seconds total) with enhanced turbulent mixing to make sure that everything is burned.

In the initial phase of study, only fuel oils or fuel oil spiked with low concentrations of selected non-toxic chemicals will be burned in the research combustor. No hazardous waste will be handled until we have received a RCRA Part B permit.

Figure 3 shows the top view for the combustion chamber section. The combustion chamber is designed for a normal load of three million Btu/ hour and a three second residence time at 30% excess air. An additional one second residence time is provided by the afterburner section. The maximum load is five million Btu/hr. The normal operating

temperature is between 1,600 to 2,200°F and the maximum operating temperature is 2,500°F. A series of nine thermocouples is permanently installed along the combustion chamber to monitor the transverse temperature profile continuously.

The combustion chamber of the research combustor consists of five sections. The first section is a burner support section which can be changed easily to adapt to different size or design burners. There are three combustion sections so that special test set-ups can be installed. For example, simulated boiler tubes may be installed in the third combustion section for fouling and slagging studies. Corrosion coupons may be installed for material of construction studies. The fifth section is the end cover with a viewing port. The combustion chamber is lined with Durablanket (a low-density firebrick) for fast heat up so that minimum time is wasted in start-up period and minimum thermal shock damage is experienced by the firebrick.

The combustion chambers are mounted on three skids. The section on the first skid has twelve, 10-inch sampling ports. At the center of the 10-inch port is a smaller 3-inch sampling port. The sections on the second and third skids have twelve, 4-inch sampling ports each. The sampling ports can be used for either non-intrusive laser

diagnostic studies or for intrusive probe sampling studies. The effects of residence time can be studied by obtaining samples at different ports along the combustion chamber. In this mode of operation, long overall residence time and high destruction efficiency can be assured at the stack at all times.

Figure 4 shows the block diagram for the complete system. Fuel tanks, a combustion air blower (1,500 SCFM and 35-inch water pressure), and a burner management system are skid-mounted for maximum flexibility. All process fluid (air, steam, fuel) flow rates and pressures are measured in order to have total control of the system operation.

The research burner which we are using for the initial phase of the research is called a "movable-block swirl generator" (2). The swirl generator is designed to be able to deliver combustion air at any ratio of radial and tangential flows. Advantages of this device are that it makes change of swirl intensity to any desired level during burner operation possible.

The research combustor has a complicated burner management system with several interlock loops to assure safe operation. It also has an emergency shutdown system which will shut down all fuel feeds automatically in case

any one of the following conditions occurs:

- o Loss of flame.
- o Low combustion air flow.
- o High or low fuel gas pressure.
- o High thermal oxidizer pressure (loss of ID fan).
- o High or low thermal oxidizer temperature.
- o Low liquid waste feed pressure.
- o Low steam or air atomization pressure.
- o High stack CO level (for hazardous waste feed).

A special water-quenched and water-cooled probe (14) is used for hot flue gas sampling in the combustion chamber. A special suction pyrometer probe (1) with water cooling is used for radial temperature profile measurement in the combustion chamber.

RESULTS

This research program is designed to obtain some empirical correlation from statistical analysis of statistically designed test results. With the knowledge generated from the studies, we can provide scientifically-based recommendations to the designers and operators to help them identify problems for an operating incinerator and provide design basis for new incinerators. The technology is also applicable in burning waste in boilers or process furnaces.

We expect that we can provide the following in-

formation from research to be conducted with the liquid-injection combustion research facilities.

1. Spray nozzle selection.
2. Best fuel mist and combustion air mixing pattern for a particular fuel (chemical waste).
3. Burner selection and performance evaluation.
4. Selection of optimum operating conditions.
5. Combustion tests to assess special combustion problems associated with a particular waste: such as boiler tube corrosion and fouling, refractory attacking, and special pollutant emissions.

An experimental program is being conducted now and we expect to have some preliminary data in the near future.

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Disclaimer

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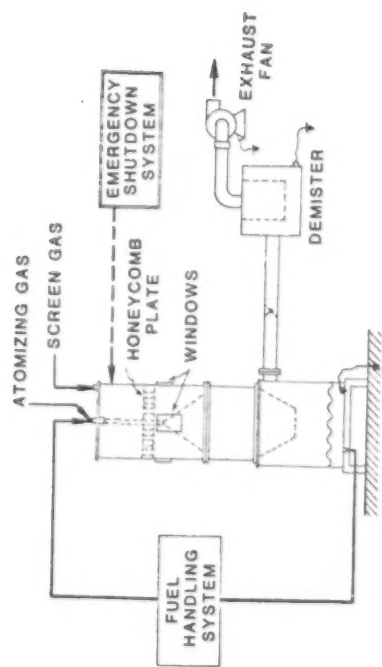


FIGURE 1. SCHEMATICS OF THE FUEL ATOMIZATION PILOT FACILITY

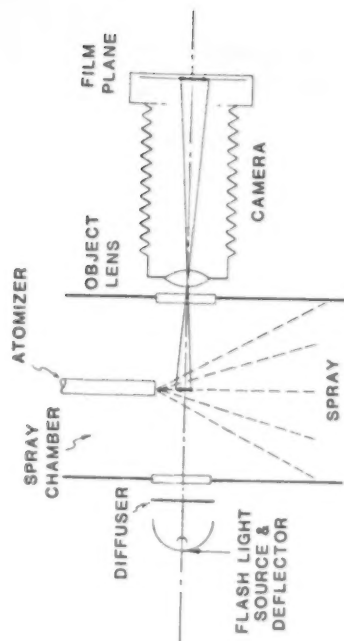


FIGURE 2. OPTICAL SYSTEM FOR FLASH SHADOW PHOTOGRAPHY

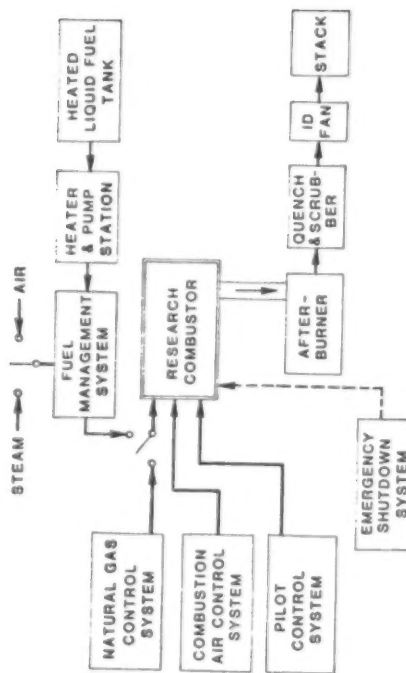


FIGURE 4. BLOCK DIAGRAM FOR THE RESEARCH COMBUSTOR

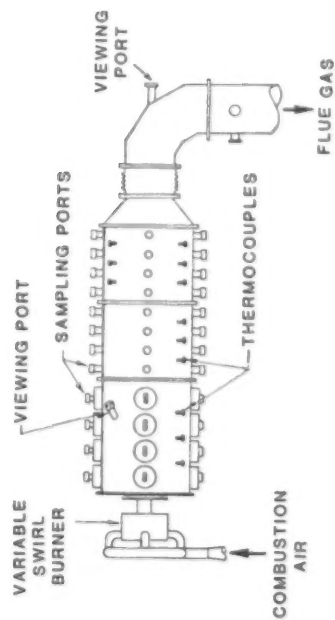


FIGURE 3. UNION CARBIDE RESEARCH COMBUSTOR - TOP VIEW

FATE OF POLYNUCLEAR AROMATIC COMPOUNDS DURING SEWAGE SLUDGE INCINERATION

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ABSTRACT

Sewage sludge accumulates biorefractory compounds such as heavy metals and toxic organics, which may pose problems if subsequent disposal options are not well managed. While the fate of heavy metals during sludge incineration has been well defined, little data is available regarding the fate of toxic organics. The prime objective of this study was to determine the fate of seven selected polynuclear aromatics during full-scale sludge incineration. The results indicated that, with the exception of dibenzofuran, destruction efficiencies for the target compounds ranged from 95.03% to 99.98% at a maximum furnace temperature of 786°C. In general, the destruction efficiency of a compound increased as its boiling point increased and as the number of benzene rings is contained increased. This suggests that in multiple hearth furnaces, operated countercurrently, compounds with low boiling points are volatilized and swept out of the incinerator without significant destruction occurring. The data also indicates that atmospheric emissions are more significant than aqueous emissions. The ratio of atmospheric to aqueous emissions varied from 2:1 for carbazole to greater than 20:1 for dibenzofuran. Generally, about 0.5 to 5% of the polynuclear aromatics in the sludge feed were released atmospherically with 0 to 1.5% discharged aqueously.

INTRODUCTION

Incineration is widely used for the ultimate disposal of sewage sludges, with approximately 40% of Canadian sludges (Schmidtke, 1981) and about 20% of U.S. sludges (Bunch, 1981) being disposed in this manner. Sewage sludge accumulates biorefractory compounds such as heavy metals and toxic organics,

which may pose problems if subsequent disposal options are not well managed. While the fate of heavy metals during sludge incineration has been well defined, (Campbell et al., 1982; Dewling et al., 1980) little data is available regarding the fate of toxic organics. Canadian (IJC, 1983) and U.S. (U.S. EPA, 1982) surveys of sewage sludges have indicated that polynuclear aromatic hydrocarbons are

frequently found to be present at relatively high concentrations. For this reason polynuclear aromatics (PNA's) are receiving considerable attention from a sludge management viewpoint. Sewage sludge from Hamilton, Ontario, was sampled and analyzed as part of Environment Canada's "Toxics Screening Study of Municipal Sewage Treatment Plants" conducted during 1981/82. This survey revealed the sludge contained relatively large concentrations of organic contaminants, especially PNA's. Consequently, Hamilton sludge is being used extensively for Environment Canada's ongoing studies aimed at determining the effect of various sludge management options on toxic organics' fate and mobility. The assessment of organic emissions from the Hamilton STP incinerators is thus just one component of Environment Canada's overall toxics assessment program.

STUDY OBJECTIVES

The prime objective of this study was to determine the fate of seven selected priority organics during multiple-hearth sewage sludge incineration. A second objective was to assess the suitability of two stack gas sampling techniques for the seven target compounds, which included acenaphthylene, fluorene, fluoranthene, pyrene, benzo-a-pyrene, (B-a-P), dibenzofuran and carbazole.

DESCRIPTION OF HAMILTON'S SLUDGE PROCESSING TRAIN

The City of Hamilton is served by a single sewage treatment plant with a design capacity of approximately 400 000 m³/d (90 mgd). Sewage sludge is currently being

produced at a rate of about 60 dry tonnes per day.

Primary and waste activated sludge are anaerobically digested prior to mechanical dewatering (vacuum filters) and subsequent incineration. Two Envirotech BSP multiple-hearth furnaces are used for sludge incineration. Each unit comprises nine alternating in/out hearths, six metres in diameter. The units are rated at 9 000 kg of wet sludge per hour, at a nominal 20% total solids and 75% volatile content. Both units are natural gas fired on hearths 3, 5 and 7. Sludge is fed via a weigh belt from the top of the furnace (hearth #1) and moves downward through the drying, burning and cooling zones prior to being discharged as ash at the bottom of the furnace. Rabble arms move the sludge from hearth to hearth. Off gases are quenched and scrubbed prior to being discharged, via an ID fan to the stack. Quench/scrubber water (68 m³/h to each unit), which is secondary effluent from the STP, is used to slurry the bottom ash and transport it to the impoundment lagoon. A schematic of the Hamilton STP incinerators is shown in Figure 1.

SAMPLING AND ANALYTICAL METHODS

Feed and effluent streams from the incinerators were sampled during a four day period in September 1982. Samples of feed sludge, bottom ash, scrubber water and stack gases were collected during the 4-hour steady-state run on each of the four consecutive sampling days (September 15-18). Sampling locations are shown on Figure 1. The sludge feed, common to both incinerators, was sampled via grab methods each hour during the steady-state period. These samples were composited to represent the

sludge fed during the sampling period. Grab samples of ash and scrubber water were also collected each hour and composited. Stack gas was sampled using two stack sampling trains using both wet and dry collection trains. For each system, isokinetic sampling was carried out along a multipoint traverse of the stack. The wet collection train used ethylene glycol as the primary collection medium, while the dry train used an Amberlite XAD-2 sorbent cartridge. Details of the stack gas sampling are presented elsewhere (EPS, 1983).

Composited samples of sludge, bottom ash and scrubber water were analysed for the target organics by the Analytical Services Section of the Wastewater Technology Centre, while the stack gas samples were analysed by the River Road Laboratory in Ottawa. Sludge and bottom ash were extracted with acetone-hexane in a soxhlet apparatus while the scrubber water was extracted with methylene chloride in a 1 litre separatory funnel. Solid samples from the stack gas monitoring were also soxhlet extracted while liquid samples were extracted using separatory funnels. All extracts were analysed by GC/MS techniques.

RESULTS

Complete sampling of all streams was successfully effected on three of the four sampling days (September 15, 16 and 17), and results for these three days are detailed below. On September 18th only stack gas sampling was conducted and results for the amberlite train are not available. The results are subdivided to show

operating, analytical and emission data.

Operating data for the sampling period

The operating conditions of each incinerator were monitored and logged on a hourly basis during each four hour steady-state run, with the exception of wet sludge feed rate, which was monitored continuously. The average operating conditions for the two incinerators for the three test periods is shown in Table 1. On September 15th, a ruptured ash transport line forced the run to be terminated after 1 1/2 hours. Also, during this run only 84% of isokineticity was achieved, which is outside the normal accepted range of $100 \pm 10\%$. Nonetheless, it can be seen that operating conditions were similar during all three sampling periods. The two exceptions appear to be a higher furnace temperature and stack gas particulates on September 15th. The high particulate loading on September 15th is a direct result of not sampling isokinetically. Sludge loading to both units ranged from 61 to 75% of design (based on wet sludge feed rate) during the three day test period. It should be noted that the feed was lower in both total and volatile solids than the values assumed for design capacity calculations. Hearth temperature profiles are shown in Figure 2. The profiles for the 3 test periods also show that for some unknown reason, hearth 6 temperature on September 15 appears abnormal.

Analytical Results

The structure and some of the physical properties of the seven target PNA's are shown in Table 2.

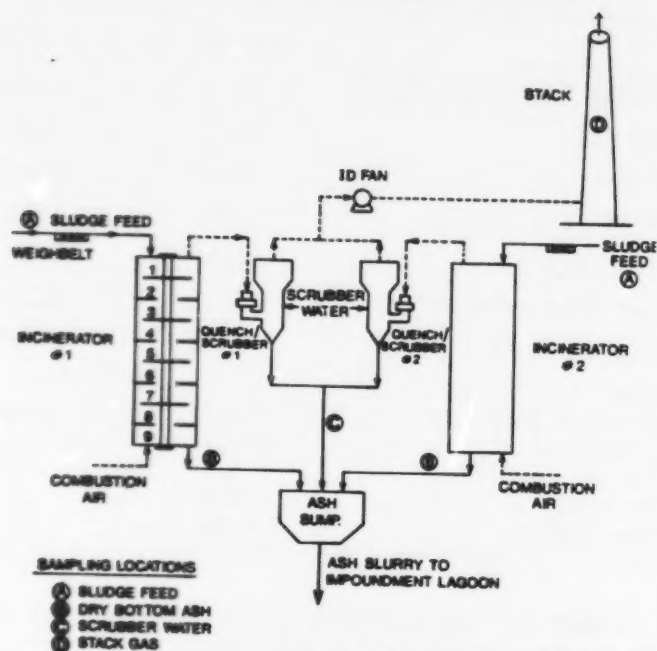


Figure 1. Schematic of Hamilton Incinerators

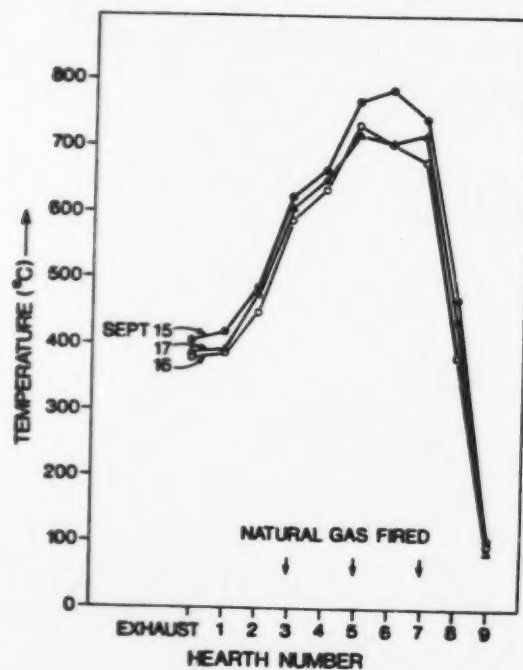
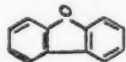
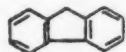
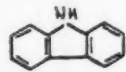
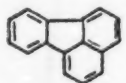
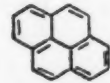
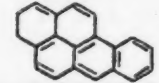


Figure 2. Hearth Temperature Profiles

TABLE 1. INCINERATOR OPERATING CONDITIONS

Parameter	Sept.15/82	Sept.16/82	Sept.17/82
Total wet sludge feed rate (kg/h)	13530	11102	11243
Sludge solids (%)	15.8	15.8	15.8
Volatile content (%)	46.0	46.0	46.0
Dry sludge feed rate (kg/h)	2138	1754	1833
Ash production (kg/h)	1154	947	990
Scrubber water flow rate (m ³ /h)	134.1	134.1	134.1
Max. hearth temperature (°C)	786	732	722
Stack gas data			
- O ₂ concentration (vol. %)	12.7	12.8	12.7
- flow rate (m ³ /min)	450.7	473.5	426.9
- velocity (m/s)	3.8	3.2	2.9
- temperature (°C)	116	66	63
- particulates (kg/h)	4.05	1.42	0.95

TABLE 2. STRUCTURE AND SELECTED PHYSICAL PROPERTIES OF TARGET PNA'S

Compound Name	Structure	Boiling Point (°C)	Aqueous Solubility (mg/L)	Ionization Energy (ev)
Acenaphthylene		266	3.93	7.76
Dibenzofuran		287	**	7.90
Fluorene		294	1.98	7.89
Carbazole		355	**	7.57
Fluoranthene		375	0.26	7.80
Pyrene		393	0.14	7.41
Benzo-a-pyrene		495	0.0038	7.12
Not available.				

As indicated, an objective of the study was to assess the collection efficiency of two gas sampling trains, namely a wet collection system using ethylene glycol and a dry train using Amberlite XAD-2 cartridges. Results from these two collection trains are shown in Table 3. Neglecting the results from September 15th (not isokinetic) it is apparent that the Amberlite train generally collects more PNA's than the ethylene glycol train. With the exception of carbazole and B-a-P, the PNA concentration measured using the Amberlite train were several times higher than the same species measured with the ethylene glycol train. In addition, the distribution of PNA in the various components of each train showed the Amberlite to be superior to ethylene glycol. For these reasons, subsequent stack gas data shown are those generated using the Amberlite train.

The results of the analyses conducted on the various samples collected during the three test periods are shown in Table 4. All of the bottom ash samples contained non-detectable (ND) levels of the target PNA's (detection level 0.1 µg/g). The data in Table 4 indicate that sludge quality (with respect to the target PNA's) was uniform during the three test periods. The only exception is that B-a-P was not detected in the sludge on September 16th. Since B-a-P was detected in the stack gas, this sludge analysis is suspect. This conclusion is supported by MOE analyses of sludge samples taken concurrently (Rush and Taylor, 1983). These sludge analyses are in general agreement with the ones generated in this study.

Scrubber water analyses indicate low levels of dibenzofuran, fluoranthene, pyrene, carbazole and fluorene were present. Analysis of the STP final effluent, which is used as raw scrubber water indicates only trace quantities of these compounds are present (Rush and Taylor, 1983).

QA/QC on the sludge, ash and scrubber water samples indicated recoveries of the target PNA's ranged from 49% to 214%. The average recovery data for these three matrices are shown in Table 5.

The replicated sludge samples were spiked at 50 µg/g, the ash samples at 25 µg/g and the scrubber water at 60 µg/L. It can be seen that while recoveries did vary, the values reported are considered acceptable for the levels of contamination encountered in these matrices and are representative of recoveries reported in the literature. Note however that the sludge, ash and scrubber water analyses reported are not corrected based on this recovery data.

Mass emission data

Based on the incinerator operating conditions (Table 1) and the analytical data (Table 4), mass balances around the incinerator system were determined. These results for the three test periods are shown in Table 6.

The destruction efficiency (DE) for each compound for each sampling day is also shown in Table 6. The DE is defined as:

$$DE = \frac{(\text{contaminant feed rate} - \text{scrubber emission rate} - \text{stack emission rate}) \times 100}{\text{contaminant feed rate}}$$

TABLE 3. STACK GAS CONCENTRATION DATA ($\mu\text{g}/\text{m}^3$)

Compound	September 15		September 16		September 17	
	Ethylene Glycol	Amberlite	Ethylene Glycol	Amberlite	Ethylene Glycol	Amberlite
Acenaphthylene	23.1	8.4	2.9	9.6	9.3	8.5
Dibenzofuran	166.9	53.6	0.7	67.3	22.9	95.4
Fluorene	49.1	16.0	7.1	25.2	8.5	27.2
Carbazole	32.5	14.9	17.5	12.7	26.2	6.
Fluoranthene	102.9	43.1	4.2	49.9	11.4	58.0
Pyrene	29.3	17.8	1.2	10.6	3.4	17.6
Benzo-a-pyrene	2.9	2.0	1.9	0.1	0	0.5

TABLE 4. ANALYTICAL RESULTS

Compound	September 15			September 16			September 17		
	Sludge*	Scrubber Water†	Stack Gas*	Sludge	Scrubber Water	Stack Gas	Sludge	Scrubber Water	Stack Gas
Acenaphthylene	4.9	ND	8.4	2.1	ND	9.6	5.6	ND	8.5
Dibenzofuran	4.4	1	53.6	2.5	1	67.3	5.3	1	95.4
Fluorene	14.4	<1	16.0	8.3	<1	25.2	16.4	1	27.4
Carbazole	6.7	trace	14.9	3.4	trace	12.7	10.0	trace	6.6
Fluoranthene	77.0	3	43.1	52.2	2	49.9	77.1	3	58.0
Pyrene	60.0	2	17.8	38.9	<1	10.6	57.3	1	17.6
Benzo-a-pyrene	36.6	ND	2.0	ND	ND	0.1	57.2	ND	0.5

*Concentration expressed as $\mu\text{g}/\text{g}$ †Concentration expressed as $\mu\text{g}/\text{L}$ •Concentration expressed as $\mu\text{g}/\text{m}^3$

TABLE 5. RECOVERY DATA FROM SLUDGE, ASH AND SCRUBBER WATER SAMPLES

Compound	Percent Recovery		
	Sludge	Bottom Ash	Scrubber Water
Acenaphthylene	62	49	66
Fluorene	83	76	81
Fluoranthene	114	75	71
Pyrene	97	97	80
Benzo-a-pyrene	214	148	140

It can be seen that individual PNA feed rates to the incinerators varied from a low of 3.68 g/h for acenaphthylene to a maximum of 164.63 g/h for fluoranthene. By contrast, stack emission rates varied from 0.003 g/h for benzo-a-pyrene to 2.444 g/h for dibenzofuran. Destruction efficiencies for the PNA's varied from 91.74% to 99.98%, with the exception of dibenzofuran, which exhibited destruction efficiencies as low as 53.39%. The results achieved during the three test periods are very consistent, especially taking into account the non-isokineticity of the stack gas analyses generated on September 15th.

Average destruction efficiencies for the seven PNA's are plotted as a function of their boiling points (Figure 3) and ionization energies (Figure 4). It appears that destruction efficiency increases non-linearly with increasing boiling point. This is to be expected for a multiple hearth furnace operated in countercurrent mode with sludge addition on hearth one. As the sludge is heated, volatile compounds are vaporized and swept to the stack with combustion air. Thus, a compound like benzo-a-pyrene, with a boiling point of 495°C, would progress much farther down the incinerator before being vaporized. Once vaporized, it would then be exposed to a more aggressive thermal regime (higher temperature, longer residence time) than would, say, dibenzofuran. The correlation of DE with ionization energy indicates that thermal stability increases with increasing ionization energy, which is to be expected.

The average PNA destruction

data, and the percentage discharged via the stack and scrubber water, are shown in Table 7. Since the stack data generated on September 15th was not collected isokinetically, the averages shown in Table 7 do not include the September 15th values.

The data in Table 7 highlight the fact that with the exception of dibenzofuran, DE's for all PNA's were greater than 95%. There are no emission standards for PNA's from combustion sources in Canada, however EPA standards for hazardous wastes, which excludes sewage sludges, do require a minimum DE of 99.99% for "principal organic hazardous constituents" (Federal Register, 1982). The emission data in Table 7 also confirm that air emissions are far more significant than aqueous emissions.

There are very few documented cases of PNA fate during incineration with which to compare this study's results. A cement kiln operated in Sweden, using tar as an auxiliary fuel, was able to assess PNA fate. At an operating gas temperature of >1400°C, 99.998% destruction of total PNA's was effected (Trovaag, 1981). The University of Dayton Research Institute (UDRI) has conducted laboratory-scale thermal decomposition studies on selected PNA's in free flowing air (Rubey, 1982). Their results are shown in Table 8. This data indicates that PNA's exhibit considerable thermal stability. The data also indicates that naphthalene and chlorinated naphthalenes are more stable than the other PNA's studied. Surprisingly, as the number of aromatic rings increase, the thermal stability of the compound appears to decrease, i.e., the order of stability decreases from naphthalene to anthracene to triphenylene to to benzo-a-pyrene.

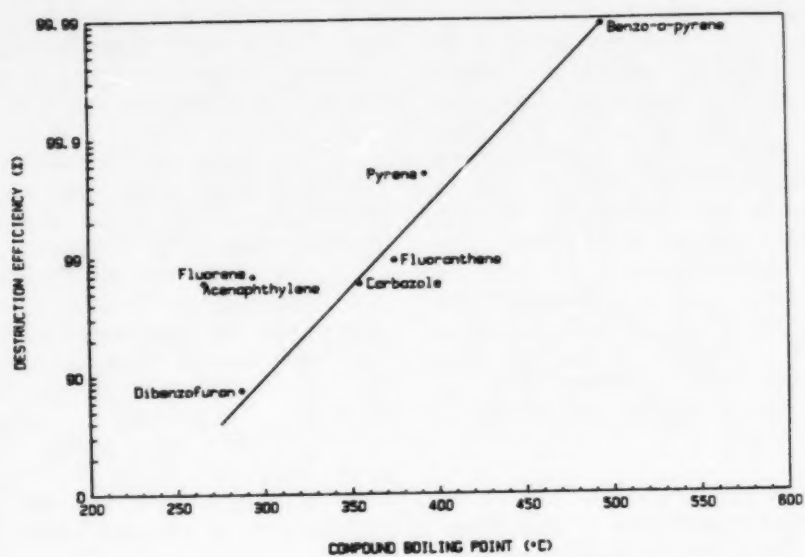


Figure 3. PNA Destruction versus Boiling Point

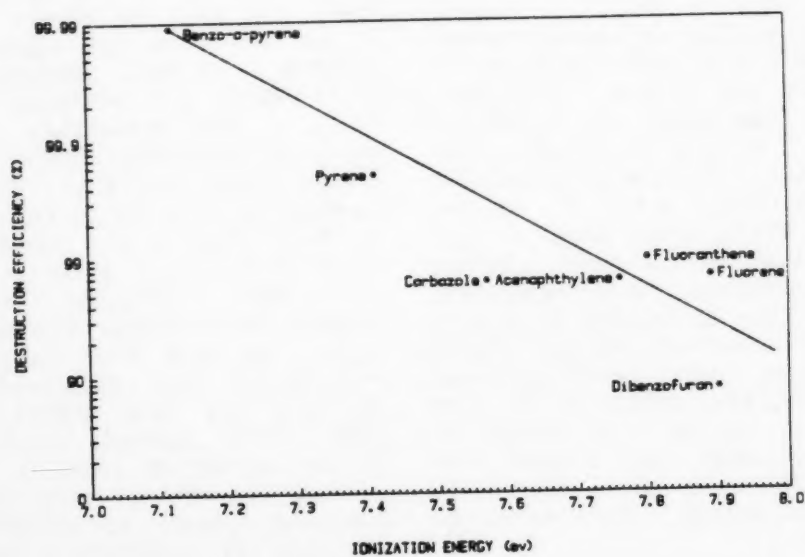


Figure 4. PNA Destruction versus Ionization Energy

TABLE 6. INCINERATOR MASS BALANCE DATA

Compound	September 15				September 16				September 17			
	Mass flow rate (g/h)			DE (%)	Mass flow rate (g/h)			DE (%)	Mass flow rate (g/h)			DE (%)
	Sludge	Stack	Scrubber Water		Sludge	Stack	Scrubber Water		Sludge	Stack	Scrubber Water	
Acenaphthylene	10.48	0.227	ND	97.83	3.68	0.273	ND	92.58	10.16	0.218	ND	97.85
Dibenzofuran	9.41	1.449	0.134	83.17	4.39	1.912	0.134	53.39	9.72	2.444	0.134	74.71
Fluorene	30.79	0.433	<0.134	98.16	14.50	0.716	<0.134	94.14	30.06	0.697	0.134	97.24
Carbazole	14.33	0.403	<0.134	96.25	5.97	0.361	<0.134	91.71	18.33	0.169	<0.134	98.35
Fluoranthene	164.63	1.166	0.402	99.05	91.50	1.418	0.268	98.16	141.32	1.486	0.402	98.66
Pyrene	128.28	0.482	0.268	99.42	68.20	0.301	<0.134	99.36	105.03	0.451	0.134	99.44
Benzo-a-pyrene	78.25	0.054	ND	99.93	ND	0.003	0.134	--	104.85	0.013	ND	99.98

TABLE 7. AVERAGE PNA DESTRUCTION/DISTRIBUTION DATA*

Compound	Average DE (%)	Percent in Stack Gas	Percent in Scrubber Water
Acenaphthylene	95.22	4.78	0
Dibenzofuran	64.05	34.35	1.60
Fluorene	95.69	3.63	0.68
Carbazole	95.03	3.49	1.48
Fluoranthene	98.41	1.30	0.29
Pyrene	99.40	0.44	0.16
Benzo-a-pyrene	99.98	0.02	0

*Excluding September 15th data

TABLE 8. LAB SCALE THERMAL DESTRUCTION PROFILES FOR SELECTED PNA'S (RUBEY, 1982)

Compound	Percent destruction at 2 second gas retention time				
	400°C	600°C	650°C	700°C	725°C
Benzene	0	0	15	89.8	98.5
Naphthalene	0	0	NA	77	85.0
Monochloronaphthalene	0	0	16	69	81.0
1,2 Dichloronaphthalene	0	0	29	76	83.0
Anthracene	0	47	71	NA	99.83
1,2,3,4 Tetrachloro-naphthalene	0	0	30	67	90.0
Triphenylene	0	27	36	94	99.50
Benzo-a-pyrene	0	36	49	96.5	99.79

This trend is supported by the results generated in the present study, which found benzo-a-pyrene to be the least thermally stable compound. The UDRI data does indicate thermal stability as the PNA's, in their vapour state, are exposed to the high temperature zone. It is therefore significant that vapour-phased thermal stability appears to decrease as the number of rings is increased.

SUMMARY AND CONCLUSIONS

The results from this study indicated that, with the exception of dibenzofuran, destruction efficiencies for the target PNA's ranged from 95.03% to 99.98% at a maximum furnace temperature of 786°C. In general, the thermal stability of a compound decreases as the number of benzene rings it contains increases.

The data also indicates that under the conditions evaluated atmospheric emissions are more significant than aqueous emissions. The ratio of atmospheric to aqueous emissions varied from about 2:1 for carbazole to 20:1 for dibenzofuran. Generally about 0.5 to 5% of the PNA's present in the sludge feed are released atmospherically, with 0-1.5% discharged aqueously.

Stack gas sampling has indicated that for the target compounds the dry collection train, using Amberlite XAD-2 cartridges, was superior to the wet train using ethylene glycol as the absorbent.

The results from this survey suggest that atmospheric emission of PNA's from the Hamilton sludge incinerators amount to roughly

60 kg/yr. Current modifications to the incinerators are, however, likely to reduce these emissions.

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Disclaimer

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